

ON THE ROLE OF INDIUM UNDERLAYS
FOR THE PREVENTION OF THERMAL GROOVING
IN THIN GOLD FILMS

By

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Preliminary studies have shown that grain boundary grooving in thin Au films is prevented by inserting an indium underlay between gold film and substrate. The objectives of this work was to investigate the mechanisms for the prevention of grain boundary grooving in In/Au composite films by comparing the microstructural evolutions of pure Au films with In/Au composite films during isothermal annealing.

Microstructures were characterized in terms of grain size, grain size distribution, texture and surface morphology utilizing TEM, XTEM, SEM and X-Ray diffraction. The chemical reactions and the distribution of the phases were monitored by SAD in TEM, and by AES sputter profilings.

It was found that the principal mechanisms to prevent grain boundary grooving in In/Au composite films are as follows:

- 1) Indium underlays modify the microstructure of Au films by randomization of the orientation of the grains, refinement of the grain size, uniformity of the grain size distribution and roughening of the surface of the gold films.
- 2) Indium is redistributed on gold films and forms In_2O_3 on the free surface and in the gold film during air annealing.
- 3) The In_2O_3 on the surface "caps" the surface of gold film and limits the mass transport process during annealing.
- 4) The In_2O_3 in the gold film, presumably residing near grain boundaries, impedes the grain growth by pinning the grain boundary migration.

Additionally, the critical conditions, where grain boundary grooves reach the substrate, were derived from geometrical consideration. The critical ratio of the thickness to grain diameter for Au films was calculated to be 0.07 using experimental values for the surface energy and the grain boundary energy from literature.

CHAPTER 1 INTRODUCTION

The continuing trends of increasing complexity of integrated circuits have placed severe demands on the improved reliability of the microelectronic devices. A significant fraction of reliability problems in the microelectronic devices have been attributed to the failures in thin film metallizations that interconnect individual components. Aluminum is the most widely used principal metallization material for providing necessary contacts and interconnections. Despite the considerable improvements to increase the lifetime by alloying with copper and silicon, aluminum metallizations are still riddled by one dominant failure mechanism, such as electromigration, which limits the reliability of the integrated circuit interconnections [1-5].

The future trends towards further miniaturization with an attendant decrease in the line width and the thickness of the metallizations favor a shift from aluminum metallization to gold metallizations because of their greater resistance to corrosion and lower susceptibility to electromigration. Gold metallizations have been known to have a longer life time under DC stressing, which might be attributed to the difference in activation energy for electromigration being about 50 to 200% higher than that of aluminum [6-9].

However, it has been shown that several other failure mechanisms, such as grain boundary grooving and thermotransport, also contribute significantly to the failure of gold metallizations. In particular, the grain boundary grooving which is driven by capillarity (surface tension) has been known to be quite detrimental to the stability of gold thin film metallizations [10-13].

A grain boundary groove, or thermal groove, is formed when a grain boundary meets the free surface and its depth deepens with time. In a sufficiently thin metallization film, this groove may reach the substrate, leading to voids in the film or to an open circuit. Even when the grooves do not extend all the way to the substrate, the decrease in cross sectional area will cause increased Joule heating and current crowding which results in a concomitant increase in temperature and electromigration rate, so that the groove area will be the preferred sites for the failure [14-16].

Hummel et al. have shown that indium underlays between gold and the substrate inhibit the development of grain boundary grooving during heat treatment in gold thin film metallizations [17,18]. Although stabilizing effects of the indium on the grain network of gold films have been observed, the conclusive explanation why indium underlays impede grain boundary grooving has not been provided.

The objective of this dissertation is to investigate the mechanism for the inhibition of grain boundary grooving of gold thin films by the addition of indium underlays.

In order to achieve this objective, microstructure evolutions, chemical reactions and re-distribution of the phases during deposition

and the isothermal heat treatment are monitored. Microstructures are characterized in terms of grain size, grain size distribution, texture, and surface roughness, utilizing TEM (Transmission Electron Microscope), SEM (Scanning Electron Microscope), X-ray diffraction and XTEM (Cross-Sectional Transmission Electron Microscope). The chemical reactions such as oxidation and the intermetallic compound formation and the distribution of the phases are accomplished by SAD (Selective Area Diffraction) in TEM and AES (Auger Electron Spectroscopy) sputter profiling.

Three types of specimens have been prepared: 1) pure Au films, 2) In/Au composite films annealed in air, 3) In/Au composite films annealed in hydrogen gas. The effect of indium underlays upon the microstructure of gold films during deposition is studied by comparing the microstructure of "as deposited" pure gold films with the microstructure of "as deposited" In/Au composite films. The effect of In_2O_3 on a microstructural evolution during annealing has been investigated by comparing the microstructures of annealed pure Au films with the microstructures of annealed In/Au composite films.

Additionally, some theoretical considerations that include instability conditions for thin films caused by grain boundary grooving as a function of the grain size and the groove angle and the parameters which might change the evolution of grain boundary grooves in gold thin films are discussed.

It will be shown that In_2O_3 on the surface and in the grain boundary are responsible for stabilizing the surface structure and for

inhibiting the grain growth, respectively, which in turn reduce the grain boundary grooving of gold thin films during heat treatment.

CHAPTER 2 THEORETICAL BACKGROUND

2.1 Brief Review of Driving Forces for the Mass Transport

There are several different kinds of driving forces to cause mass transport in thin films. In general, the action of a driving force on atomic motion can be written [19]

$$J_i = - D_i \nabla C_i + F (D_i / f k T) C_i$$

where J_i = the atomic flux of i th constituent

C_i = the concentration of i th constituent

D_i = the diffusivity of i th constituent

f = the correlation coefficient appropriate to the mechanism responsible for the motion, and

kT has its usual meaning.

The first term represents the action of diffusion. The second term shows the influence of an external driving force.

Driving forces derived from the electric current (electrotransport) and by the thermal gradient (thermotransport) are briefly reviewed below. Mass transport driven by capillarity may also be important in thin films; capillarity effects will be discussed separately in section 2.2.

2.1.1. Electrotransport (Electromigration)

Electrotransport, or alternatively electromigration, is the phenomenon of mass transport arising from the driving force of electric field or electric current. In electrotransport, the driving force is considered to be the sum of two effects: 1) electrostatic interaction between the electric field and the ionic core of the atoms, and 2) a friction force between these ions and the flowing charge carriers, which is often called the electron wind force. Accordingly, the driving force can be expressed by [20]

$$F = Z^* |e| E = (Z_{el}^* + Z_{wd}^*) |e| E$$

where Z^* = the effective charge number
 e = the charge of an electron, and
 E = the electric field.

From the theoretical considerations, Z^* is given by

$$Z^* = \pm z [1 - \gamma (\rho_d/N_d) (N/\rho) |m^*| / m^*]$$

where z = the electron - atom ratio of the material
 $(\rho_d/N_d) (N/\rho)$ = the ratio of the specific
 resistivity of the moving defects
 to that of the lattice
 m^* = the effective mass, and
 γ = a numerical constant = 0.5.

Usually the electron wind force is dominant and thus the mass transport is presumed to occur in direction of the electron flow.

The flux of atoms due to electrotransport is given by

$$J_i = N_i D_i / k T \quad Z^* e E$$

where N_i is the number of i th atoms per unit volume.

2.1.2. Thermotransport (Thermomigration)

Thermotransport, or thermomigration, is the transport of mass due to a temperature gradient. The driving force for the thermotransport can be expressed by [21]

$$F_i = - Q_i / T \nabla T$$

where Q_i = the heat of transport of i th constituent, and
 ∇T = the temperature gradient = $\partial T / \partial x + \partial T / \partial y + \partial T / \partial z$.
 Q is the energy which flows per unit mass transported; it has three contributions [22]:

$$Q = Q_{int} + Q_{el} + Q_{ph}$$

where Q_{int} = the intrinsic contribution due to the motion of atoms under the static temperature gradient,
 Q_{el} = the contribution due to the electron-moving atom interaction under thermo electric field, and
 Q_{ph} = the contribution due to the heat carrier interaction (phonon scattering).

The atomic flux along the temperature gradient can be written as

$$J_i = - N_i D_i Q_i / k T^2 \nabla T.$$

The net transport of matter will be toward lower temperature if Q_i is positive and toward higher temperature if Q_i negative.

2.2. Capillary Induced Mass Transport

2.2.1. Introduction

When polycrystalline metals and alloys are heated at an elevated temperature the shape of the external surface will be altered. The changes in surface morphology are caused by mass transport driven by the capillarity; they have been analyzed rigorously in the theories of thermal grooving and morphological instability. Thermal grooving theory, or grain boundary grooving theory, deals with the formation and the evolution of the groove which is formed at the intersection of a grain boundary with a free surface. Morphological instability theory deals with the conditions where the original geometry becomes unstable due to perturbations driven by capillarity. Both thermal grooving and morphological instability are caused by the surface curvature, which is related to the chemical potential. However, the curvature, thus the driving force is discontinuous at the grain boundary for the case of the thermal grooving while it is continuous for the case of the morphological instability.

In section 2.2.2., thermal grooving theories involving several different mass transport mechanisms are presented. Morphological instability theories for different geometries are given in section 2.2.3.

2.2.2. Theories of Thermal Grooving

A thermal groove is formed at the intersection of a grain boundary and the free surface as the surface energy and the grain boundary energy establish an equilibrium satisfying the relation

$2 \gamma_s \sin \theta = \gamma_g$, where θ is the equilibrium groove angle, γ_s is the surface energy and γ_g is the grain boundary energy (Figure 1).

The ultimate motivation for the formation of the thermal groove is the minimization of the total free energy of the system by reducing the interfacial free energy [23,24]. Although the grain boundary and the surface may quickly achieve the proper equilibrium angle where they intersect, the groove will generally continue to grow. Thermodynamically, the growth will continue until the system reaches its lowest free energy by eliminating the grain boundary. Mechanistically, the growth occurs in response to the chemical potential gradient which is caused by the curvature of the groove profile. The Gibbs-Thompson formula relating the curvature and the chemical potential shows that a curved surface has chemical potential that is different from a flat surface. The gradient in chemical potential drives atoms from a point of higher chemical potential to one of lower chemical potential, with the result that the groove deepens with time [25].

Assuming isotropic surface properties, Mullins developed a theory of thermal grooving in which mass transport occurred under the solitary action of: 1) evaporation-condensation mechanism, 2) surface diffusion mechanism, and 3) volume diffusion mechanism [26]. The differential equations describing the evolution of the groove profiles are derived using small slope approximation.

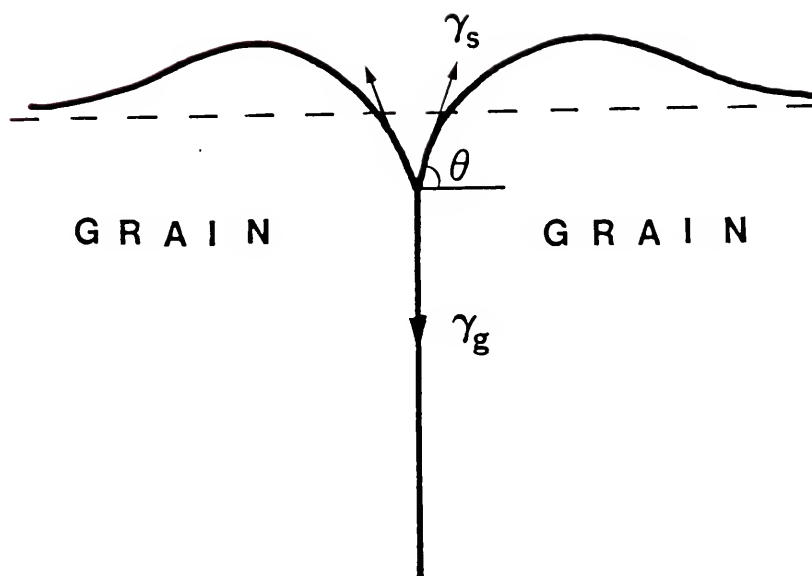


Figure 1. Profile of Thermal Grooving

The shapes of the groove profiles and the dimensional characteristics produced by each transport mechanism are shown in Table 1.

Table 1. Shapes of Groove Profiles for Various Mechanisms of Mass Transport

MECHANISM	SHAPE OF PROFILE
Evaporation and Condensation	No Maxima
Surface Diffusion	Maxima
Volume Diffusion	

The shape of the profile depends upon m , which is the tangent of the equilibrium angle, but is independent of time. Furthermore, the linear dimensions of the fixed shape are proportional to $t^{1/2}$, $t^{1/4}$ and $t^{1/3}$ for evaporation-condensation mechanism, surface diffusion mechanism and volume diffusion mechanism, respectively.

The three mechanisms of mass transport may operate simultaneously [27,28]. The relative importance of each mechanism depends upon the experimental conditions, which may affect the vapor pressure, the diffusivity and the diffusion distance. It is found that surface diffusion is the dominant process in the initial stage whereas the volume diffusion and evaporation-condensation mechanisms are important at later stages.

The predictions of Mullins theory fit reasonably well with computer calculations and the experimental data [29-31]. Huang and Lin have extended the Mullins theory to cases where ridges or notches are present on the initial surface [32]. It is shown that the grooving takes place only if the initial slope of the notch is less than $\gamma_g/2\gamma_s$, or if the initial surface has a ridge at a grain boundary.

The thermal grooving theory in a system where a loss of matter due to free evaporation or corrosion occurs simultaneously with surface diffusion has been treated numerically [33,34]. It is shown that the groove evolution is not steady state; thus the groove shape is time dependent and also that the groove depth and the width do not follow a $t^{1/4}$ law. It is suggested that free evaporation and corrosion effects should not be ignored for temperatures greater than $0.65 T_m$ or for

lower temperatures when the reaction between the adsorbed gases and the specimen occurs.

Without the assumption of the small slope approximation and the steady state evolution, a numerical analysis of the groove evolution for a plane and a wire has been performed [35]. It is predicted that the groove evolution can lead to the failure of the wire only by surface diffusion, which indicates the significant effect of geometry on the evolution of thermal grooving.

Most thermal grooving theories for thin films deposited on a substrate have been studied in the system where the films are stressed at high current densities. The thermal groove profile therefore is influenced, not only by temperature but also by electromigration. Using the approach of Mullins, Ohring has derived an equation for the groove profile caused by the applied electric field [36]. It is shown that the unidirectional electromigration flux establishes the asymmetry in the profile which is characterized by a fixed shape where linear dimensions change with time as $t^{1/4}$. In the case where the temperature gradient is dominant the groove depth varies with time as $t^{1/3}$. When the divergence of the mass flux induced by the electromigration is not equal to zero ($\nabla J \neq 0$), a local mass depletion or accumulation occurs, which accelerates thermal grooving. The electrotransported mass is depleted at or carried from a grain boundary groove, upsetting the equilibrium angle and thereby establishing a driving force which promotes further groove deepening.

Effects of annealing and electromigration on grain boundary grooving has been investigated in a bicrystal film which is

isothermally annealed and subsequently stressed at a high current density [37]. The combination of fluxes from capillarity-induced surface diffusion and electromigration-induced grain boundary diffusion is shown to cause open circuit failures by developing severe mass depletion and accumulation at the grain boundary groove.

2.2.3. Theories of Morphological Instability

The morphological changes of the surface driven by capillarity may cause the instability of the original geometry. The break-up of a long cylinder into spheroidal particles, the blunting of a field emission cathode and the rupture of a wire by thermal grooving are examples of this phenomenon [38-41].

Instability conditions are strongly dependent upon the geometry, dominant mass transport mechanism, the surface energy, the amplitude and the direction of the perturbation. While small perturbations in a nearly planar surface will decay with time to make the flat surface stable, some perturbations in a nearly cylindrical or spherical surface increase their amplitudes with time to make the original surface unstable.

First-order perturbation analysis has been treated by Rayleigh for inviscid fluids assuming the cylinder of infinite length [42]. Analogous treatment has been performed by Nichols and Mullins for different geometries [43]. For an infinite cylinder with longitudinal perturbation by surface diffusion the following instability conditions are obtained.

For any longitudinal perturbation of wavelength less than λ_0 ,

which is $2\pi R_0$, the cylinder is stable, i.e. such perturbations decay with time. For $\lambda > \lambda_0$, the cylinder becomes unstable, i.e. such perturbations increase in amplitude with time. For $\lambda = \lambda_M$, the wave length at which the perturbation develops the maximum value, the cylinder breaks up into a line of particles with spacing λ_M .

The mechanism of break-up of plate-like particles has been also predicted; a platelet will first develop a doughnut-shaped rim, which is essentially a curved cylinder by a bulging process along its edges. This rim will in turn break up into a ring of spheres separated by λ_M , by the process discussed above. The experimental support for this mechanism has accomplished by Yen and Coble [44]. The spheroidization of semi-infinite rods has been treated with a numerical method in which the initially uniform circular section is spheroidized into a series of egg-shaped particles. Nichols has analysed a finite cylinder with hemisphere ends and has calculated the critical length to diameter ratio (L/D) of 7.2. Below this value only one spheroidal particle results; above it the particle breaks up into two or more parts [45].

The energetics and the kinetics of the instability of a thin film where an initially uniform film, which has been deposited on a substrate, breaks up into an array of beads or islands, has been studied by Srolovitz and Safaran [46,48]. They have calculated the instability condition for a thin film with respect to large amplitude perturbations, namely holes and islands using non linear perturbation analysis. To evaluate the shape of the film, a quasi-static approximation is employed, i.e. determine the shape of the film by minimizing the energy of the system with respect to film shape. It is

found that holes which exceed a critical size, which is proportional to the ratio of the thickness to equilibrium contact angle, grow and eventually disconnect the film. For a potential source of these large perturbations the grain boundary groove, especially at the vertex, where three grain boundaries meet, is proposed.

CHAPTER 3 EXPERIMENTAL PROCEDURES

3.1. Film Preparation

The pure Au and the In/Au composite films were prepared by using a high vacuum deposition technique.

The substrates on which the films were deposited were optically flat, commercial grade fused quartz plates ($2.5 \times 3.5 \times 1 \text{ mm}^3$), which were polished on one or both sides. Films were deposited on the polished side. Impurities of the quartz substrate were as follows:

Al_2O_3 : 60 - 100 ppm, Fe_2O_3 : 3-5 ppm, K_2O : 3 ppm

TiO_2 : 5 ppm, Na_2O : 4 ppm, Ca : 0.5 ppm, B : 0.3 ppm

Prior to deposition the substrates were examined with the aid of an optical microscope to discard the ones with gross defects such as scratches, seeds and bubbles. The substrates were then ultrasonically cleaned in the following sequences:

- 1) Alconox detergent (7.3% phosphorous by weight, pH 9.0 - 9.5) and water in order to remove water-soluble and some organic contaminants including oils, greases, soils and carbon products.

- 2) Micro and de-ionized water in order to remove water-soluble contaminants which were introduced by the detergent.

3) Reagent grade acetone, a semi-polar solvent, acting as a vapor degreaser.

4) Reagent grade alcohol, a less polar solvent containing fewer inherent impurities used to continue the cleaning action initiated by the acetone wash.

The substrates were then subjected to a stream of dry air and re-examined optically for flaws. The substrates were mounted in spring-loaded holders that enabled the placement of a molybdenum mask over the substrate. These holders were then placed in the vapor deposition chamber for film deposition.

Prior to opening the vacuum chamber to load the substrates and the source materials, several heating tapes were wrapped around the chamber in order to minimize impurity adsorption along the walls and the constituent parts of the chamber. After the appropriate substrates and source materials were placed in the chamber, the system was immediately closed and pumped down. A mechanical pump was used to bring the pressure in the chamber to 1.5×10^{-1} Torr within 5 minutes. This cut-off pressure and the use of a zeolite-filled absorption trap minimized the backstreaming of water and the hydrocarbon molecules from the mechanical pump oil back into the chamber. Laboratory grade nitrogen was then bled into the chamber to reduce the partial pressure of oxygen and water vapor. This process was repeated several times before turning on the adsorption pump. A liquid N_2 cooled absorption pump then reduced the chamber pressure 1.5×10^{-1} Torr to 2×10^{-3} Torr (2.6×10^{-1} Pa) by particularly reducing the partial pressures of nitrogen, carbon dioxide, water vapor and residual hydrocarbons. After

outgassing the titanium filament of a sublimation pump, the adsorption pump was closed off. Two sputter-ion pumps, in conjunction with the sublimation pump, brought the system pressure down to the deposition pressure within 3 to 5 hours. Base pressures prior to deposition were in the range of $4-6 \times 10^{-8}$ Torr ($5-8 \times 10^{-6}$ Pa).

The Au was evaporated from a Mo boat that was resistively heated by 180 amps generated by a 3 KVA power supply. The purity of Au wire was 99.999%. A sufficient amount was loaded to prevent the poor wetting of Au. Deposition was carried out with the ion pump on. Pressure during the deposition was maintained below 1×10^{-6} Torr (1.3×10^{-4} Pa). The substrates were held at room temperature but the radiation heating during the evaporation raised the substrate temperature up to about 45 deg C, which was measured by the Alumel-Chromel thermocouple attached to the substrate. Deposition rates of Au varied from 2 A/s to 9 A/s with an average rate of approximately 3.3 A/s.

For In/Au composite films, indium of 100-150 Å thickness was deposited first on the quartz substrate by applying 120 amps to a Mo boat. Indium wire of 99.99% was used as the source material. Base pressure prior to deposition of In was below 6×10^{-8} Torr (8×10^{-6} Pa) and the pressures during deposition were $1-4 \times 10^{-7}$ Torr ($1.3-5 \times 10^{-5}$ Pa). Deposition rates ranged from 2 A/s to 8 A/s with an average rate of 4.8 A/s. After deposition, about 2 to 15 minutes were required for the system to reach the base pressure, 6×10^{-8} Torr (8×10^{-6} Pa) for the subsequent deposition of Au. Gold film of 700-800 Å thickness then was deposited on the indium-covered quartz. Pressures during

deposition were $1-4 \times 10^{-6}$ Torr ($1-5 \times 10^{-5}$ Pa) and the deposition rates ranged from 2 to 8 Å/s. The thickness of the films was measured in situ with a piezo-electric film thickness monitor calibrated for gold.

Upon completion of the deposition, the ion pump was turned off and the films were stored in the vacuum chamber for more than 6 hours for cooldown. The films were inspected with an optical microscope for probable defects produced during the deposition process such as pinholes, scratches and noticeable contaminants. The specimen with defects were discarded.

3.2. Isothermal Annealing

Three annealing temperatures, namely 300, 400 and 500 C, were chosen to approximate those temperature produced during the typical electromigration tests. A 500 C anneal was chosen to accelerate any thermally activated processes. The annealing time, unless specified, otherwise was 1 hour.

The specimens were heated in a tube furnace where the temperature and the atmosphere were controlled. The furnace was pre-set to the annealing temperature and allowed to stabilize for 2 hours before the specimen was inserted.

Annealing in an oxidizing atmosphere was accomplished by heating the specimens in air. No purging step was taken. Upon completion of heating, the specimens were removed from the hot zone and were allowed to cool in air at the cold zone for 30 minutes.

Annealing in a reducing atmosphere, that is in H_2 , required several precautions due to potential oxidation of films during the heat treatment. Preliminary experimental results showed that the use of an inert gas, for example, Ar (99.999 % pure), for purging and cooling caused some oxidation. Therefore, only ultra high pure H_2 (99.999%) was used for purging, heating and cooling. For heating and cooling, the specimens were inserted into the hot zone and pulled out into the cold zone with a stainless steel rod. To avoid any oxidation, the specimen relocations were carried out while H_2 was flowing. The H_2 pressure during the heating was maintained to 4 psi (2.7×10^4 Pa). The flow rate of H_2 was controlled by monitoring the gas bubbles from an oil bath.

3.3. Characterization of Film Microstructures

3.3.1. Scanning Electron Microscopy

Surface topography of pure Au and In-alloyed Au films were examined in a JEOL scanning electron microscope JSM 35 CF. The specimens were mounted on an aluminum specimen holder (5mm in diameter) with silver paint and were dried for 24 hours before examining them in the microscope. No conducting coatings were applied.

The grain size and the grain size distribution were measured using a line intercept method, which allows calculation of the size of the grain from counting the number of intersection of a line of known length with the grains.

3.3.2. Auger Electron Spectroscopy

An analysis of the atomic species contained in the films as well as the sputter profiles for In/Au composite films were accomplished by using a Scanning Auger Microscope. Up to 8 specimens were mounted on a carousel holder in a single loading and sequentially rotated in front of the analyzer. The critical conditions for the analysis were as follows:

E-Gun beam voltage: 3 KV

Peak to peak modulation amplitude: 3 eV

Sweep rate: 3 eV/s

Detection sensitivity: 25 V

Electron multiplier: 1000 V

Base pressure: $<1 \times 10^{-9}$ Torr (1.3×10^{-7} Pa)

Pressure, Ar ion sputtering: 4×10^{-5} Torr (5.3×10^{-3} Pa)

Ion Gun beam voltage: 2 KV

Ion Gun emission current: 5 mA.

Identification of peaks in the Auger spectrum was accomplished through the combined use of a chart of Principal Auger Electron Energies and the standard spectra in the handbook [49]. Transition peaks of NVV (69 eV), MNN (404 eV) and KLL (510 eV) were used to identify Au, In and O elements, respectively. Peak to peak heights for these peaks were measured and plotted with respect to the sputter time.

The quantitative analysis, atomic concentration (%), was obtained from the calculation using the formula:

$$C_x = I_x/S_x / \Sigma (I_a/S_a)$$

where C_x = atomic concentration, %
 S_x = relative sensitivity of element X
 I_x = peak to peak height of element X
 S_a = relative sensitivity of element A
 I_a = peak to peak height of element A.

The relative sensitivity of element X was calculated from the peak to peak heights of element X and silver in the handbook. The relative sensitivities of Au, In and oxygen calculated were 0.417, 0.93 and 0.484, respectively. Atomic concentration for each elements were plotted with respect to the sputter time and these profiles were normalized to the thickness of Au films.

3.3.3 Transmission Electron Microscopy

The films were examined in a JOEL 200CX STEM operated at 200 KV. A given film for conventional top view transmission electron microscopy was floated off the quartz substrate in a 40 % concentrated hydrofluoric acid and rinsed in DI water. The floated film was then put on a standard 3mm copper grid with 100 mesh and dried in the dessicator before examination in the microscope.

A grain structure of the film was obtained by image mode and the diffraction patterns were obtained by SAD (Selective Area Diffraction) mode. The size and the distribution of the grains were measured by line intercept method. Phase identification was accomplished by measuring the distance of the diffraction spot or ring from the center (transmitted beam) and using the formula [50]:

$$R \times d = \lambda \times L$$

where R = the distance of the diffraction pattern
 d = the inter-planar spacing of a phase
 λ = the wave length of the electron
 L = the camera constant of the microscope.

3.3.4. Cross Sectional Transmission Electron Microscope

The cross sectional TEM refers to examining the specimen in cross section by TEM. That is, the surface normal of the specimen is made perpendicular to the electron beam. The preparation of cross section specimens of TEM has been described by several investigators mainly for silicon based materials [51-52]. The same type of preparation technique was adopted for annealed In/Au composite films, although several modifications had to be made for following reasons:

- 1) A very thin area is required for TEM examination for an Au based alloy because Au has a very high atomic number, which means that it is very difficult for electrons to transmit the specimen.
- 2) Since sputter rates of Au and quartz are supposed to be quite different, a uniform thinning during ion milling is difficult.
- 3) As Au has very poor adhesion to most surfaces, it is critical to apply an adhesive compound which has a good adhesion and the mechanical strength.

The specimens were prepared in the following sequence:

1. Sectioning

The specimens were sectioned into rectangular slabs that measured 2.5 mm in width and 9 mm in length. A diamond low speed wafering saw was used for this purpose. The slabs then were degreased and thoroughly cleaned by ultrasonic scrubbing in acetone.

2. Gluing

Two slabs were glued face to face into a composite by applying a thermosetting adhesive epoxy compound in between them. The epoxy compound was prepared by mixing 16g of EPOK 812, 14g of NMA (Nadic Methyl Anhydride) and 0.58g of DMP-30 (Tris dimethylaminomethyl phenol). The compound was very fluid so that a smooth and thin layer could be easily applied.

The composite was then inserted into a vise and pressure was applied by moving the crosshead toward the end plate which was made out of teflon. The vise which was designed to hold a composite together under even pressure during curing was then put into a convectional oven and cured at 70 deg C for 8 hours. Subsequently, the vise was allowed to cool for 45 minutes. Then the composite was removed from the vise by releasing the pressure. The glue on the surface of the composite was removed by slightly grinding with the sand paper.

3. Molding

For protection and handling purposes, the composite was embedded into the epoxy compound by molding. This was accomplished by filling up a rubber mold with epoxy compound, followed by inserting the composite into the mold. Care was taken not to introduce any bubbles

during inserting the composite into the mold. The mold was then put in an oven and cured at 70 deg C for 8 hours. After curing has been completed, the mold was allowed to cool for 1 hour. The molded epoxy bar which contains the composite inside was removed then from the mold.

4. Slicing and Mounting

The molded epoxy bar was sliced into several discs of 0.3 mm thickness with a diamond wafering saw. In most cases, more than 6 discs were cut from a single epoxy bar.

Up to three discs were then simultaneously mounted onto a disc holder (1 cm in diameter and 2 cm in height) on a hot plate using a crystal-bond wax.

5. Grinding

The disc holder was then inserted into a DISC Grinder by which the height of the specimen grinding was controlled with an increment of 10 μ m. The discs were ground by using a low speed rotating wheel using 600 grit self adhesive sand paper. Less than 3000 rpm was used as rotating speed. Plenty of water was supplied during grinding in order that the wax did not overheat and melt. The thickness of the disc was frequently checked with a micrometer while the discs were still attached to the disc holder. The grinding was terminated at a thickness of about 150 μ m. Both the disc holder and the DISC Grinder were cleaned thoroughly with a detergent and water. They were gently rubbed by a cotton swab during cleaning to remove any surface contaminants.

6. Polishing and Mounting

Three successive polishing steps were carried out using 1 μm diamond paste, 0.3 μm alumina and 0.03 μm alumina on separate polishing cloths. Rotation speeds were maintained below 2000 rpm. It was critical to clean the disc holder and the DISC Grinder thoroughly after each polishing step in order not to introduce scratches during polishing.

Upon completion of the final polishing and the cleaning, the disc holder was put on a hot plate and each disc was turned over to thin the other side. More crystal-bond wax was applied if necessary.

7. Grinding

The other side of the discs were ground the same way as in step 5 until the thickness was less than 100 μm . Subsequent thinning the discs from 100 μm to 20 μm was accomplished by grinding them manually with plenty of water on sand paper. Special care was taken not to apply excessive pressure during grinding. The cleaning was followed by using the same detergent and rubbing the specimen with a cotton swab.

8. Polishing and Demounting

Final polishing was accomplished with 1 μm diamond paste on polishing cloth. A 1000 rpm rotating speed and short polishing time were used to avoid breakage of the disc. Cleaning followed the same procedure as in step 7.

The disc holder was then put on a filter paper and was soaked in acetone for 20 minutes to remove any wax. As the discs were demounted from the holder, they remained on the filter paper, which was carefully

removed and dried. The discs were very fragile and were handled with utmost care.

10. Gluing

In order to improve handling in the subsequent processes and the microscope examination, the discs were glued on a standard 3 mm copper grid having a single hole of 1 mm diameter. This was accomplished by applying EPOXY(Double/Bubble), Harman Co., around the edge of the hole and putting the disc on the grid. The position of the disc was adjusted to make sure that the interface was located at the center of the grid. The copper grid was then cured in an oven at 100 deg C for 2 hours.

11. Ion Milling

The final thinning was accomplished by ion milling the specimen in a ion milling instrument with a terminator, where argon ions were accelerated with 5 KV potential, a specimen current of 3 mA and a specimen tilt of 13 degrees. The vacuum level was about 5×10^{-6} Torr (6.6×10^{-4} Pa). The terminator measured the specimen current every 10 seconds and shut off the ion milling automatically when the current reached the pre-set current. A total of 8 to 10 hours were taken before the terminator stopped the milling. Once perforation was achieved, the tilt angle was reduced to about 11 degrees for another 15 to 30 minutes ion milling without using the terminator.

Most of the cross sectional TEM examination were accomplished in Hitachi H-800 TEM (200 KV). Some of the specimens were investigated by EDX (Energy Dispersive X-ray Spectroscopy) analysis for the quantitative information of the elements.

3.3.5 X-Ray Diffraction

X-ray diffraction patterns for pure Au and In/Au composite films were obtained from an automated powder diffractometer operated at 45 KV. The position and the integrated intensity of the diffraction peak was automatically measured and recorded on the chart by data processing computer.

CHAPTER 4

RESULTS AND DISCUSSIONS

The following experiments were undertaken to study the effect of indium underlays upon microstructural evolutions of gold thin films:

- 1) annealing of pure Au films at 300 C, 400 C and 500 C
for 1 hr in air
- 2) annealing of In/Au composite films at 300 C, 400 C and 500 C
for 1 hr in air
- 3) annealing of In/Au composite films at 300 C, 400 C and 500 C
for 1 hr in hydrogen gas

4.1. Microstructure Studies of Pure Au Thin Films

4.1.1. As Deposited Pure Au Films

a) Grain structure

Figure 2a depicts the grain structure of an as deposited Au film examined by TEM. This micrograph reveals a mixture of fine and coarse grains. It is noted that, apart from the predominant grains whose mean grain diameter is about 1000 Å, much bigger grains, of a few thousand Å in diameter can be easily distinguished.

The presence of such large grains may suggest the preferential growth of large nuclei along certain crystallographic direction during deposition. The nucleation and the growth of gold evaporated on the non reacting surface, known as "non-wetting growth," has been known to form large nuclei because of the high mobility of adsorbed atoms, called adatoms, along the surface [53]. Similar grain structures have been reported by other investigators in vapor deposited gold thin films although the mean grain size was found to be different probably due to different deposition conditions [54,55].

b) Surface morphology

Very little detail of the surface structure were resolved by SEM as shown in Figure 2b, which suggested that the as deposited pure Au film had a very smooth surface. The surface roughness in the vapor deposited thin films is determined by the statistical process of nucleation and growth and the surface mobility of adatoms during deposition [56]. As the surface mobility increases, the tendency to have a smooth surface increases since the condensation can occur preferentially at the concavities and thus smoothens the surface.

The surface mobility of adatoms increases with increasing kinetic energy of adatoms and the substrate smoothness. The effect of kinetic energy on the surface mobility of evaporated gold adatoms has been studied by Chopra [57]. He showed that critical nuclei can move a considerable distance with the momentum imparted by gold adatoms.

The surface of the substrate used in the present experiment was polished. A very flat surface with little irregularities was observed by the examination of the cross section of the substrate in TEM. The

surface smoothness of the as deposited pure Au films, therefore, is believed to result from the smooth surface of the substrate and the high kinetic energy of gold atoms during deposition.

c) Texture

X-ray diffraction patterns revealed very strong $\{111\}$, $\{222\}$ peaks and a weak $\{311\}$ peak (Figure 3). SAD patterns revealed that the intensity of $\{220\}$ ring was greater than that of the $\{111\}$ ring (Figure 4).

The preferred orientation, or fiber texture, in the film can be determined by comparing the X-ray and SAD diffraction patterns with the diffraction pattern of the randomly oriented gold powders which is listed in JCPDS (Jointed Committee of Powder Diffraction Standard). The randomly oriented gold powders have the most intensive $\{111\}$ and moderately intensive $\{200\}$, $\{220\}$, $\{311\}$ peaks as shown in Table 2.

Therefore, the very strong $\{111\}$ and $\{222\}$ peaks in the X-ray diffraction patterns suggest a (111) preferred orientation in the film. Furthermore, since X-ray diffraction does occur from the crystals which lie parallel to the substrate surface, it is suggested that the (111) orientation is parallel to the substrate surface [58].

SAD patterns complement the presence of a (111) texture in the film. The fact that the intensity of the $\{220\}$ ring is greater than that of $\{111\}$ ring suggests that the incident electron beam direction is likely to be $[111]$ direction since electron diffraction in TEM does occur from the crystals which lie parallel to the incident beam

(a)


 $0.2\ \mu\text{m}$

(b)

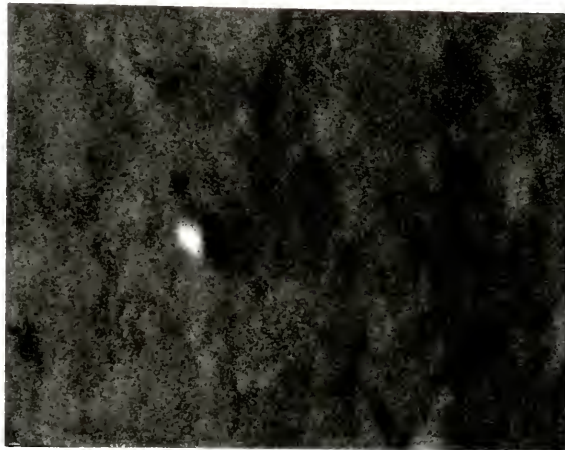


Figure 2. Photomicrographs of As Deposited Pure Au Films :
a) Transmission Electron Micrograph
b) Scanning Electron Micrograph

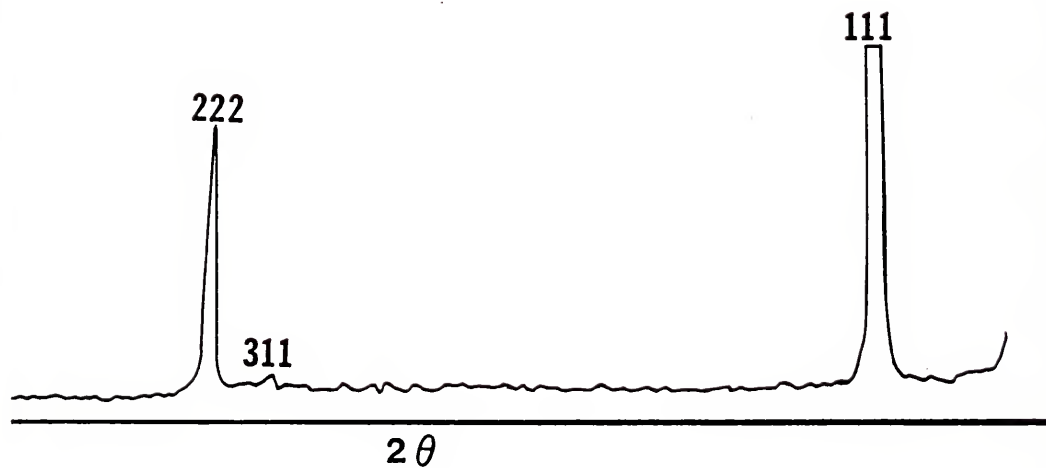


Figure 3. X-Ray Diffraction Patterns of As Deposited Pure Au Films



Figure 4. SAD Patterns of As Deposited Pure Au Films

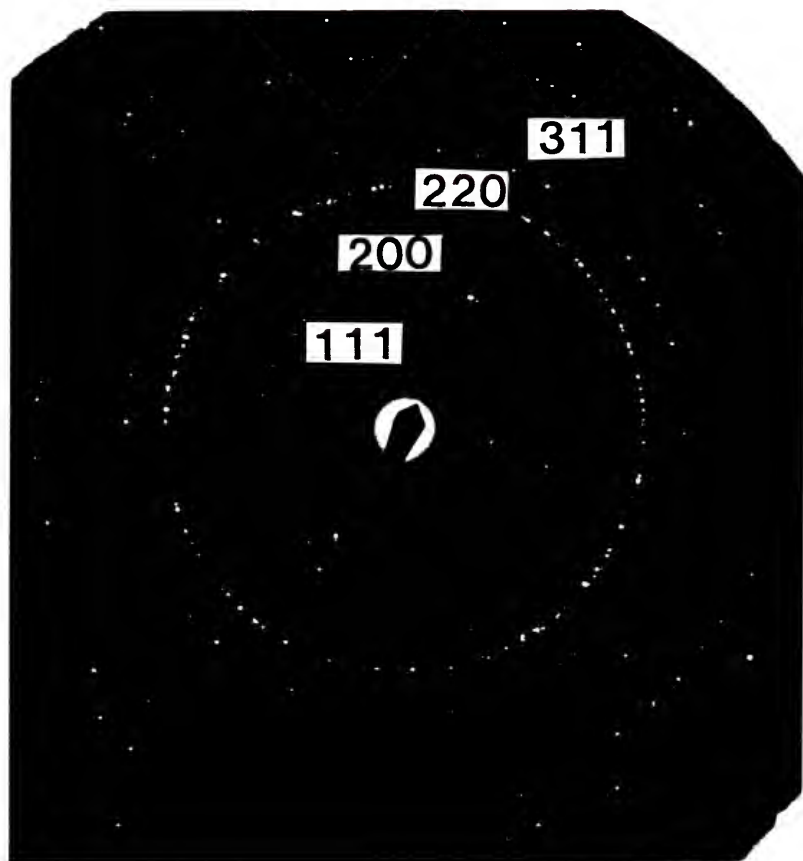


Figure 4. SAD Patterns of As Deposited Pure Au Films

Table 2. X-Ray Diffraction Patterns of Au Powders Listed in JCPDS

d, Å	$I_{hkl}/I_{111}, \%$	hkl
2.355	100	111
2.04	52	200
1.442	32	220
1.23	36	311
1.177	12	222

direction [59,60]. In summary, as deposited pure Au films have a (111) texture parallel to the substrate surface.

The preferred orientation in thin films may develop at various stages, e.g., nucleation, growth, epitaxial growth and heat treatment. When the substrate has a dominating influence on the orientation, in which the substrate energetically favors the adsorption of one geometrical arrangement atoms in nuclei over another, the epitaxial growth will be most probable [61,62]. The structure of the substrate used in the experiment, fused quartz, is amorphous. Thus, the preferred orientation during epitaxial growth is not likely to occur. The temperature of the substrate during deposition was maintained below 45 degrees C, hence texture development due to heat treatment is also disregarded. Therefore, the (111) texture in the as deposited pure Au film was likely to develop during the nucleation and growth stages.

According to the capillarity theory of nucleation, the texture will occur for the orientation which gives lower interfacial free energy, and hence a lower free energy of formation for the critical nucleus, and a much higher nucleation rate than any other orientation [63]. The (111) orientation of gold has been reported to have the lowest interfacial energy [64]. Thus, the preferred nucleation of (111) might occur during the nucleation stage.

Several empirical rules concerning texture formation during grain growth stage have shown the principle of geometric selection during growth stage. That is, in the growth of randomly oriented nuclei, only those grains will survive in which the direction of maximum rate of growth approximately coincides with the normal to the crystallization

front [65]. According to this principle, the closest-packed planes will lie parallel to the substrate if the surface mobility of adatoms during deposition is high. Since (111) is the closest-packed plane for gold, the higher rate of (111) orientation than other orientation could be achieved.

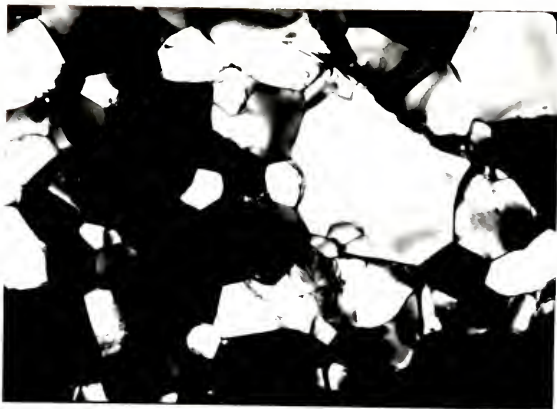
In summary, whether it is attributed to a higher nucleation rate or a higher growth rate, or due to a combination of the two, the (111) texture which is parallel to the substrate surface is likely to occur during deposition. The presence of a (111) texture is in agreement with other experiments in which gold films evaporated on the amorphous substrate had a (111) texture after deposition [66].

4.1.2. Annealed Pure Au Films

a) Grain structure

The grain structures of pure Au films annealed at 300 C, 400 C and 500 C examined by TEM are shown in Figure 5. One observes a coarse-grained structure throughout. A significant grain growth occurred during annealing as shown in Figure 6, in which the mean grain diameters are plotted with respect to the annealing temperatures. The wide scattering in the grain size indicates the wide grain size distribution. This becomes wider as the annealing temperature increases. This might be caused by the higher growth of textured grains during annealing at the expense of the small grains.

(a)



(b)

 $0.2\ \mu\text{m}$

(c)



Figure 5. Transmission Electron Micrographs of Pure Au Films
Annealed at : a) 300 C, b) 400 C, c) 500 C

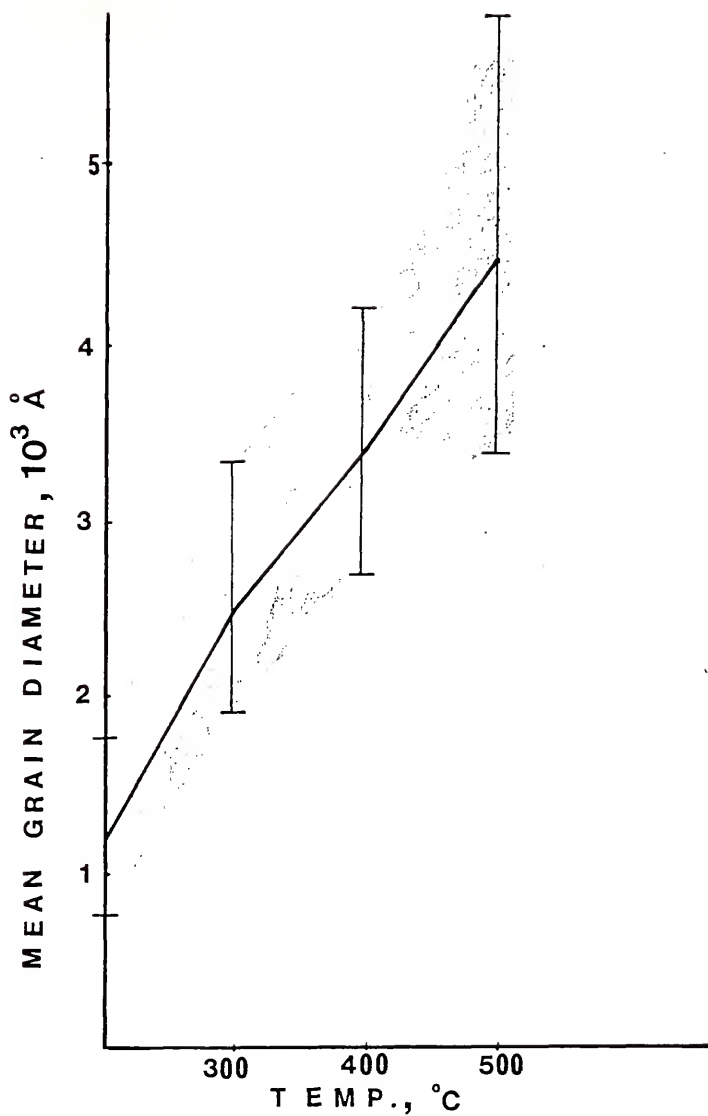


Figure 6. Mean Grain Diameters measured from Transmission Electron Micrographs of Pure Au Films Annealed at Various Temperatures

b) Surface morphology

Very significant morphological changes in the surface resulting from the grain boundary grooving and the grain growth are shown in Figure 7. Thermal grooves along the grain boundaries or at the grain boundary vertices, where three grain boundaries meet, were observed as dark lines or dark spots in the SEM micrograph (Figure 8a) and as bright lines or spots in the TEM micrograph (Figure 8b). The development of grain boundary grooving during annealing is evident and the degree of the grooving seems to increase as the annealing temperature increases.

The most severe grain boundary groove was observed in a gold film annealed at 500 C, where a hole formed at the grain boundary vertex as shown in Figure 8b. The presence of a hole at the vertex was confirmed by the fact that there was no change in the contrast of the bright spot during tilting the sample up to 45 degrees in TEM examination. Since the grain boundary grooving is caused by the capillary-induced mass transport, which is a thermally activated process, the effect of annealing temperature on the development of the groove seems quite significant. Development of similar grain boundary grooving in thin gold films annealed at elevated temperatures or stressed at high current densities has been reported [67-68]. However, large holes due to the loss of adhesion or gas bubbles entrapped during deposition were not observed in the present experiment.

(a)



(b)


0.2 μ m

(c)



Figure 7. Scanning Electron Micrographs of Pure Au Films Annealed at : a) 300 C, b) 400 C, c) 500 C

(a)


0.2 μm

(b)



Figure 8. Thermal Grooves in the Grain Boundaries and in the Grain Boundary Vertices observed by : a) SEM, b) TEM

c) Texture

X-ray diffraction patterns revealed very strong $\{111\}$ and $\{222\}$ peaks, which suggested the (111) texture parallel to the substrate surface in the annealed pure Au films (Figure 9). The change in the amount of the texture during annealing can be monitored by comparing the intensities of $\{111\}$ peaks. The change in the intensity of 111 peak for annealed pure Au films as a function of the annealing temperature is shown in Figure 10. The increase of the relative intensity as the annealing temperature increases suggests a favored development of grains with (111) orientation during annealing.

The (111) textures in the annealed pure Au films are also evident in the SAD patterns, in which the $\{220\}$ ring is more intensive than the $\{111\}$ ring, indicating that the $[111]$ direction is the incident beam direction (Figure 11). The presence of a (111) texture parallel to the substrate surface is in agreement with other experimental data, in which the (111) texture was reported in the annealed gold films [65,69].

4.2. Microstructure of In/Au Composite Films

4.2.1. As Deposited In/Au Composite Films

a) Grain structure

Figures 12a and 12b depict the grain structure of as deposited In/Au composite films examined by TEM and SEM, respectively. They reveal a uniform and fine-grained structure with a mean grain diameter of about 700 Å.

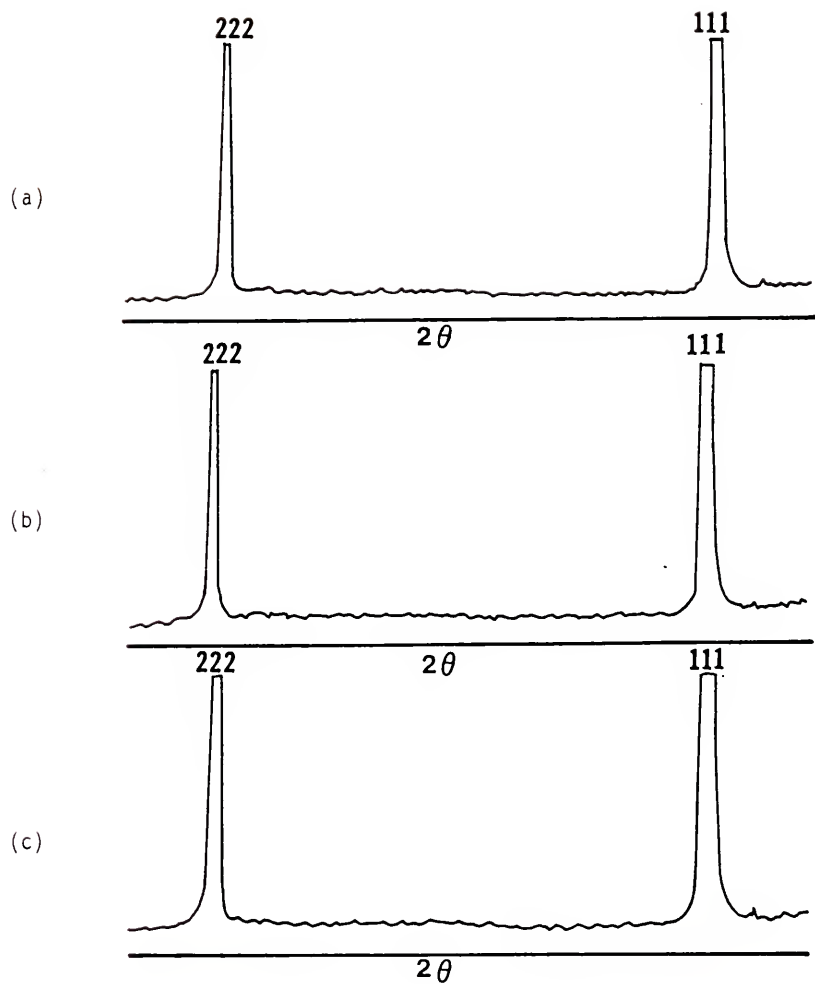


Figure 9. X-Ray Diffraction Patterns of Pure Au Films Annealed at : a) 300 C, b) 400 C, c) 500 C

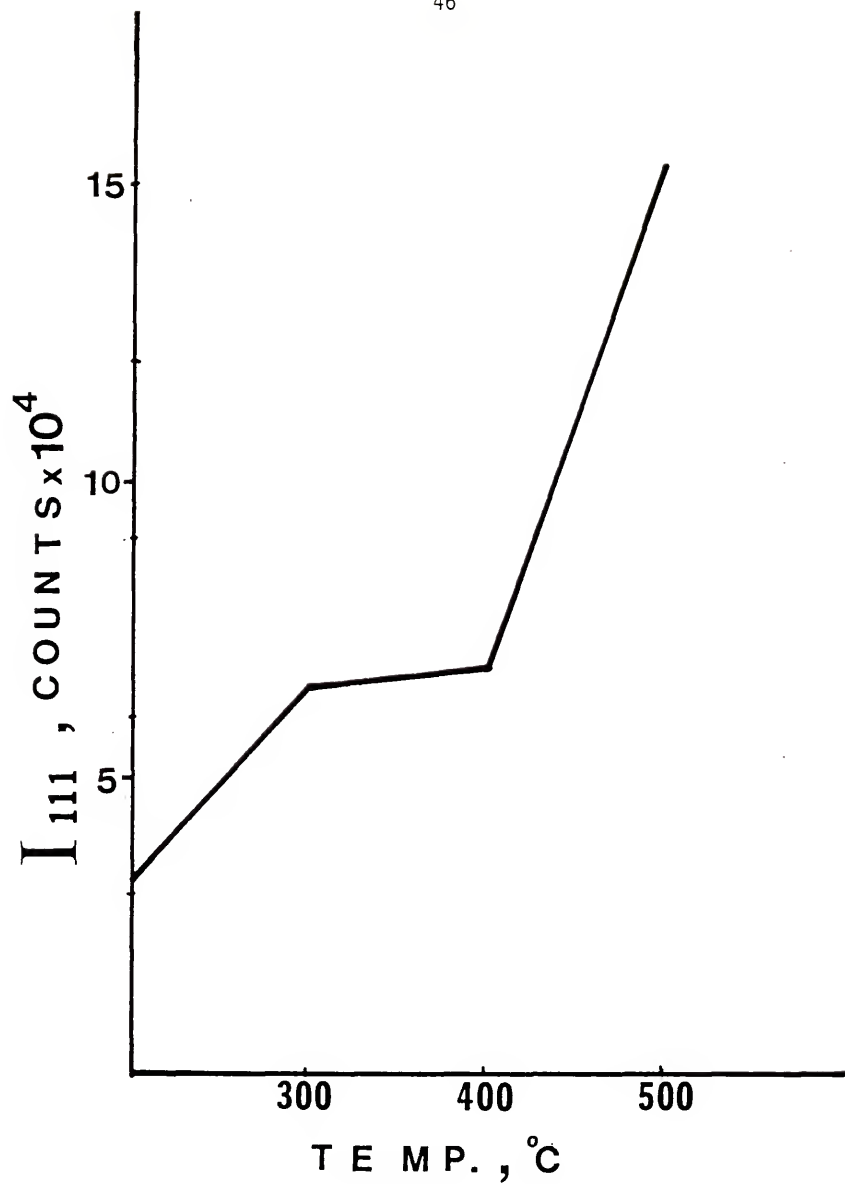
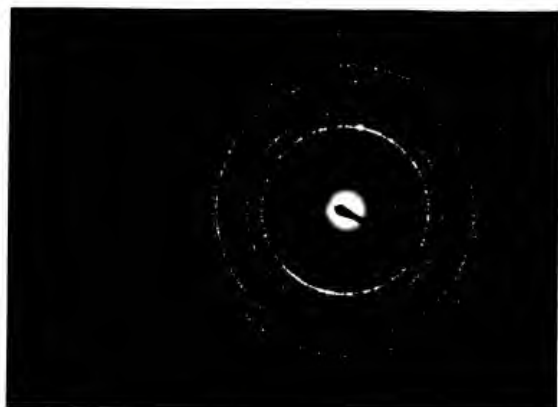
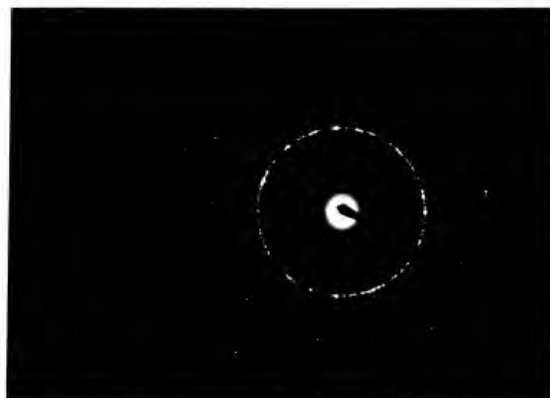


Figure 10. Intensities of (111) Diffraction of Pure Au Films Annealed at Various Temperatures

(a)



(b)



(c)

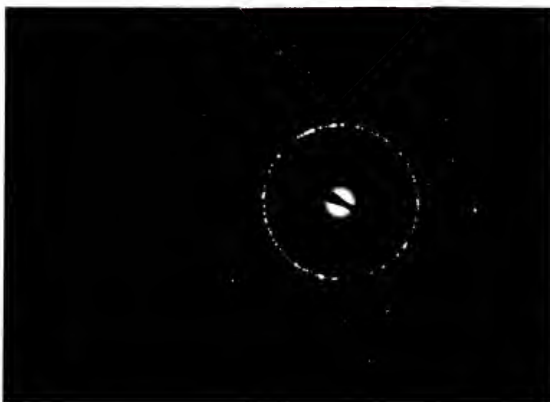


Figure 11. SAD Patterns of Pure Au Films Annealed at :
a) 300 C, b) 400 C, c) 500 C

For comparison purposes, the grain structure of a pure indium film (800 Å in thickness deposited on a quartz substrate) was examined by SEM (Figure 13). A rather uniform and fine-grained structure with a mean grain diameter of 850 Å was observed. It is easily noticed that the grain structure of the In/Au composite film is qualitatively similar to that of a pure indium film. This suggests that the microstructure of In/Au composite films may be influenced by the microstructure of the indium underlay film.

More careful examination shows some structural difference between In/Au composite films and pure In film, however. These differences are 1) the mean grain diameter of pure indium film (850 Å) is larger than that of In/Au composite film (700 Å) and 2) the pure indium film has two maxima, at about 700 Å and 1000 Å, in the grain size distribution whereas the In/Au composite film has a single maximum at about 700 Å. These differences may be attributed to grain growth of the pure indium film at room temperature and/or to the thickness effect on the grain size. Since indium has a low melting temperature, 155.4 °C, the homologous temperature, T/T_m , at room temperature is about 0.7. This is high enough to cause normal grain growth [70]. As some grains grow, the grain size distribution with two maxima may result.

The effect of the film thickness on the grain size of deposited thin films has been reported before for many systems [71-73]. The grain size was observed to increase with increasing thickness. Since the thickness of pure indium films examined was about 800 Å whereas the thickness of indium underlay in the In/Au composite film was 100 Å, a smaller grain size in the In/Au film than in the pure indium film is

expected. However, this is not generally a linear effect; i.e. the grain size of a 100 Å film is not necessarily 100 Å, but more likely about 700 Å. Considering these two effects, it is suggested that the microstructure of indium underlay affects the microstructure of the subsequent gold film during deposition.

b) Texture

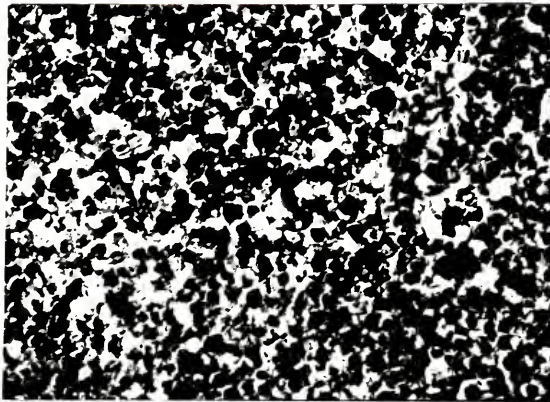
X-ray diffraction patterns revealed all possible diffractions of gold, namely {111}, {200}, {220}, {311} and {222} (Figure 14). The relative intensities of each peak with respect to the intensity of the {111} peak are compared with those of randomly oriented gold powders in Table 3. The trend is similar, which indicates that as deposited In/Au composite films have a relatively random orientation of gold grains with the tendency of the {111} texture. SAD patterns complement this information by observing the {111} ring to be the most intensive (Figure 15).

The relatively random orientation of grains in the as deposited In/Au composite film suggests the absence of a preferred nucleation and growth along a certain crystallographic direction. A decreased surface mobility of adatoms has been reported to cause the random orientation in vapor deposited thin films [74]. In summary, as deposited In/Au composite films have the random orientation of gold grains which may result from the decreased mobility of gold adatoms during deposition.

c) Surface morphology

The surface morphology of the as deposited In/Au composite film examined by XTEM is shown in Figure 16. A surface roughness similar to

(a)



(b)

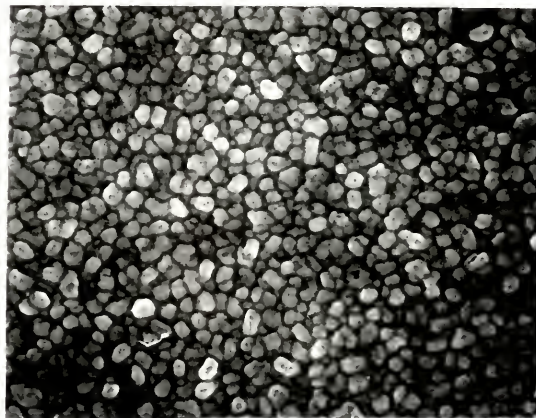


Figure 12. Photomicrographs of As Deposited In/Au Composite Films:
a) Transmission Electron Micrograph
b) Scanning Electron Micrograph

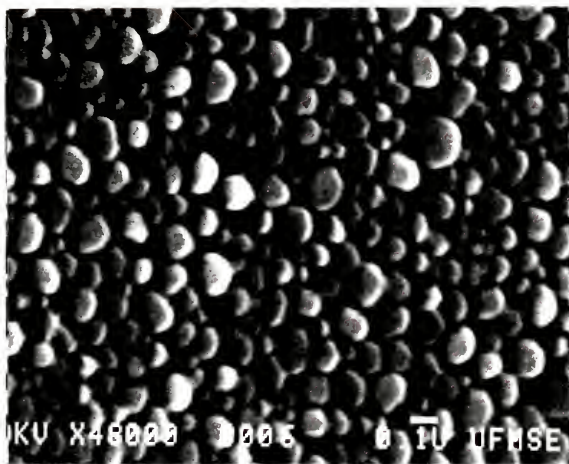


Figure 13. Scanning Electron Micrograph of Pure Indium
of 800 Å Thickness

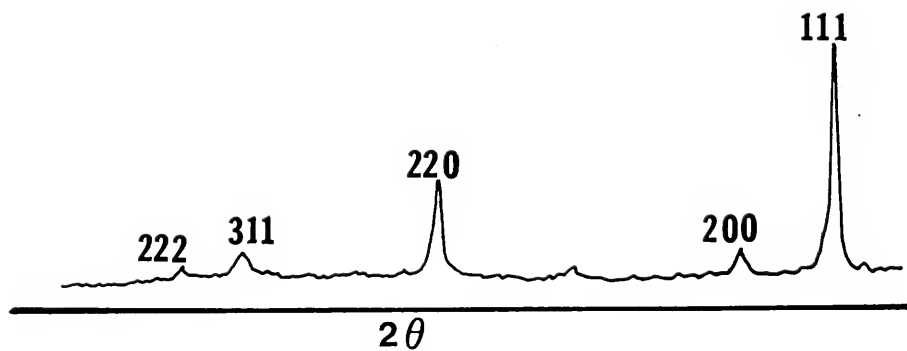


Figure 14. X-Ray Diffractions of As Deposited In/Au Composite Films

Table 3. Values of I_{hkl}/I_{111} for As Deposited In/Au Composite Films

	I_{hkl}	$I_{111}, \%$
	Au Powder	In/Au Composite
111	100	100
200	52	16
220	32	15
311	36	15
222	12	11

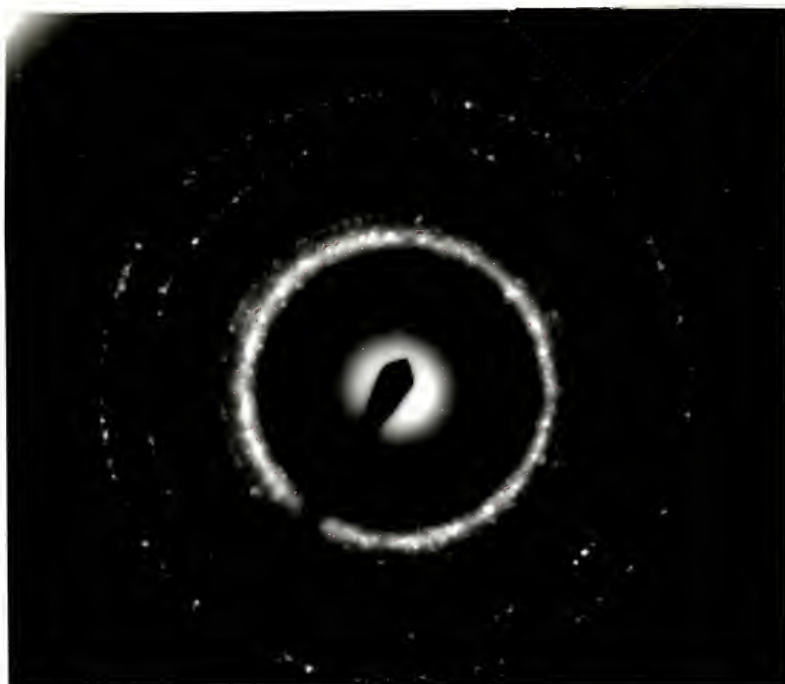


Figure 15. SAD Patterns of As Deposited In/Au Composite Films

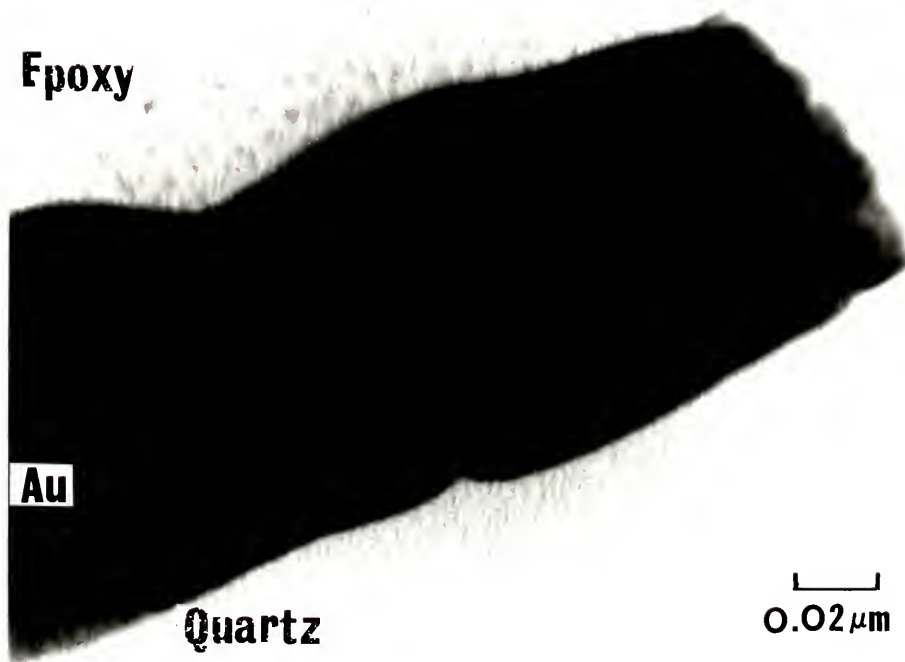


Figure 16. Cross Sectional Transmission Electron Micrograph of As Deposited In/Au Composite Films

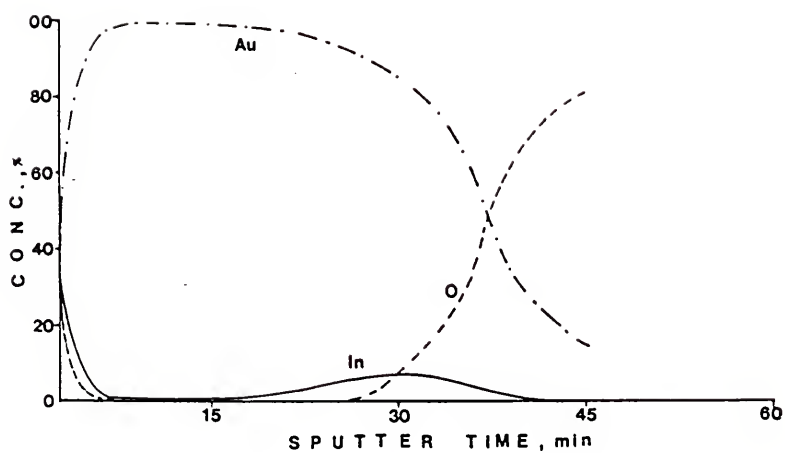


Figure 17. AES Sputter Profile of As Deposited In/Au Composite Films

Some co-deposition of indium and gold could occur either by radiation during gold evaporation or by heat conduction through the electrodes. This is possible because of the low melting point of indium. It requires only about 40% electric power compared to gold evaporation. Furthermore, the molybdenum boats were located very close together with one of their ends connected to the same electrode. However, if indium on the gold surface resulted from co-deposition of indium and gold, a uniform concentration of indium within the gold film would be expected. This has not been observed. Therefore, co-deposition of indium during gold deposition seems not to have occurred to a large extent.

Interdiffusion of indium and gold during deposition may be aided by the kinetic energy of the gold atoms which impinge upon the indium surface during gold deposition. The kinetic energy imparted in this way could promote the rapid formation of a mixed layer or intermetallic compounds during the deposition depending upon the deposition parameters such as deposition rate and substrate temperature. For example, the formation and the growth of a AuIn_2 phase in Au/In thin film couples during evaporation has been reported [76,77]. A growth mechanism was proposed which entails the rapid diffusion of indium along the grain boundaries of AuIn_2 grains to the surface. An interdiffusion during deposition, thus, might have occurred in this experiment. However, no intermetallic compounds or any other phases were observed by SAD in TEM and X-ray diffraction analysis.

Interdiffusion after deposition may occur if the indium in the underlay diffuses out to the free surface at room temperature. Rapid

diffusion of indium at room temperature has been observed by several investigators [77,78]. Furthermore, some enrichment of indium on the surface after deposition in Au/In composite films and Au-In alloy films monitored by RBS and AES has been reported [79,80]. Particularly, the accumulation of indium on the surface during AES analysis has suggested the tendency of indium surface segregation at room temperature.

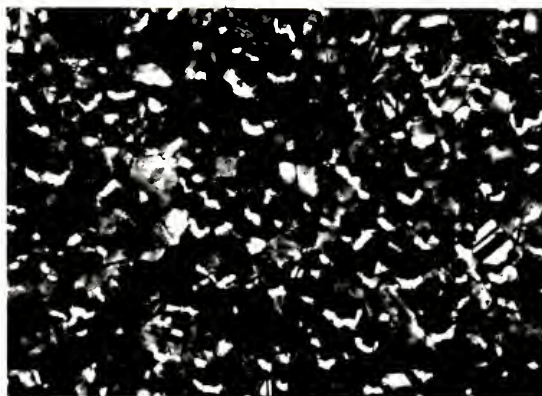
Out-diffusion of indium after deposition is most likely to occur because of high diffusivity at room temperature. The presence of oxygen on the surface may suggest the formation of indium oxide and thus the oxidation might be the driving force for the out-diffusion of indium. However, surface segregation or a concentration gradient in the Au film also could be a driving force.

4.2.2. In/Au Composite Films Annealed in Air

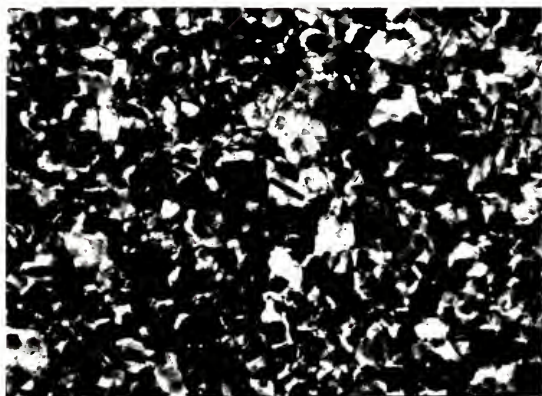
a) Grain Structure

The grain structures of In/Au composite films annealed at 300 C, 400 C and 500 C in air as examined by TEM are shown in Figure 18. The change in the mean grain diameter as a function of the annealing temperature is shown in Figure 19, where the error bars indicate the standard deviations. A true identification of grain boundaries in the images of heavily faulted polycrystalline films was difficult, and the results may be subject to some error. Nevertheless, the formation of larger grains at higher temperatures showing grain growth during annealing was evident.

(a)



(b)

 $0.2\mu\text{m}$

(c)



Figure 18. Transmission Electron Micrographs of In/Au Composite Films Annealed at : a) 300 C, b) 400 C, c) 500 C

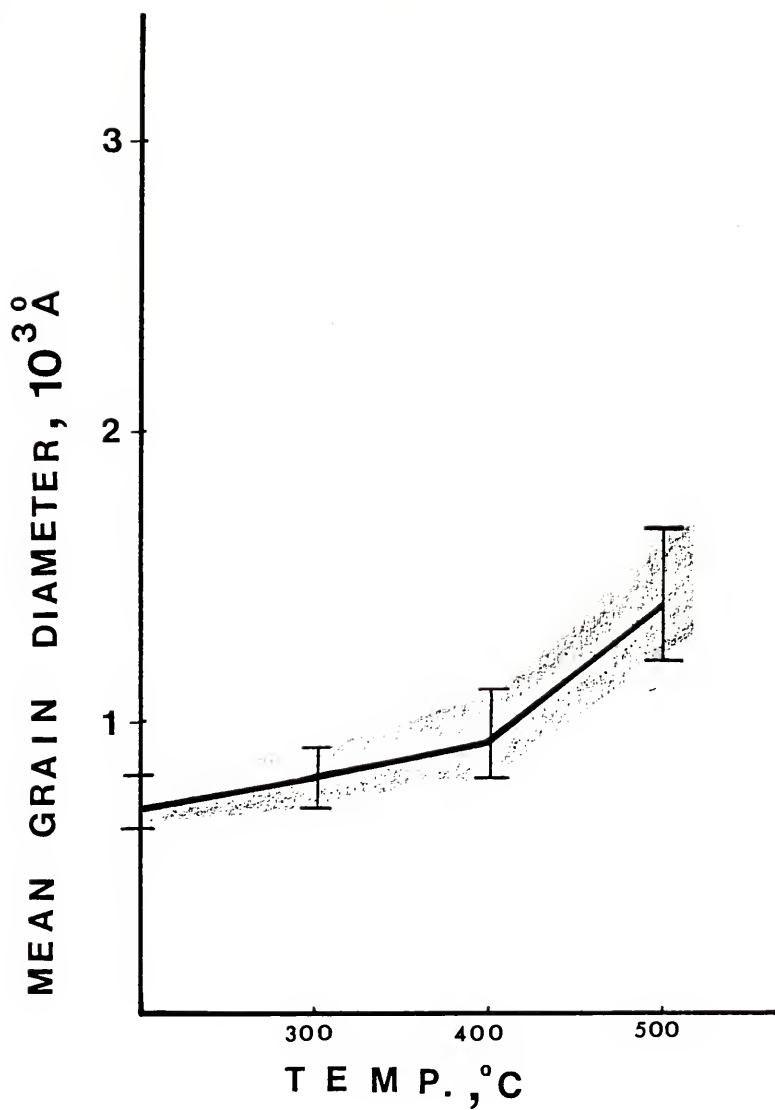


Figure 19. Mean Grain Diameters measured from Transmission Electron Micrographs of In/Au Composite Films Annealed at Various Temperatures in Air

b) Surface morphology

Very little surface structural changes and hence no significant grain boundary grooves in the annealed In/Au composite films were revealed by SEM examination (Figure 20). This will be substantiated below when XTEM results will be discussed. The mean grain diameter after annealing measured with SEM is about 700 Å, which is the same as in the as deposited In/Au composite film. This could be interpreted that no grain growth occurred during annealing, which is contradictory to the result of our TEM examination in which the grain growth was observed.

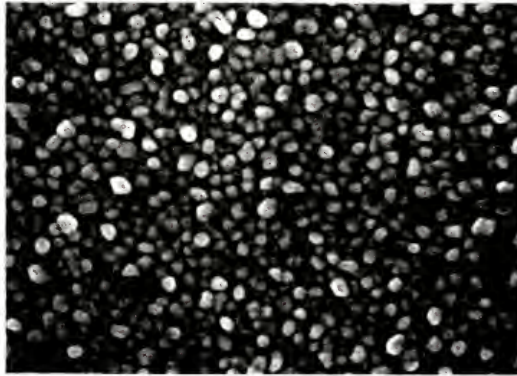
The apparent difference between the surface structure observed by SEM and the internal structure observed by TEM can be explained by considering some model structures:

1) Model A involves small grains of 700 Å in diameter and large grains of few thousands Å in diameter at the bottom of these small grains as shown in Figure 21a.

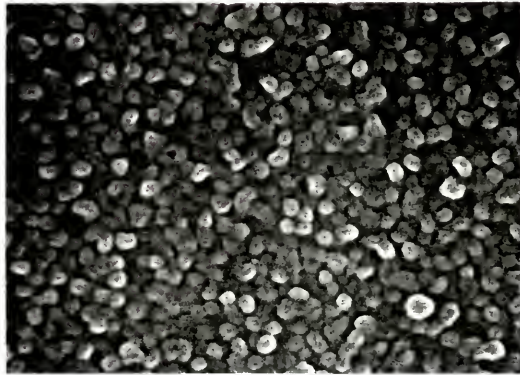
2) Model B involves large grains of about 1500 Å in diameter having rough surfaces whose sinusoidal "perturbation" wavelength is about 700 Å as shown in Figure 21b.

Image formation in SEM is achieved by the topographic contrast resulting from secondary electrons which are emitted from the specimen surface [81]. The topographic contrasts, therefore, in model A would be caused by the fine grain structure on the surface whereas those in model B would be caused by the surface roughness. Since the dimension of the small grains in model A and the wavelength of the sinusoidal

(a)



(b)



0.2 μm

(c)



Figure 20. Scanning Electron Micrographs of In/Au Composite Films Annealed in Air at : a) 300 C, b) 400 C, c) 500 C

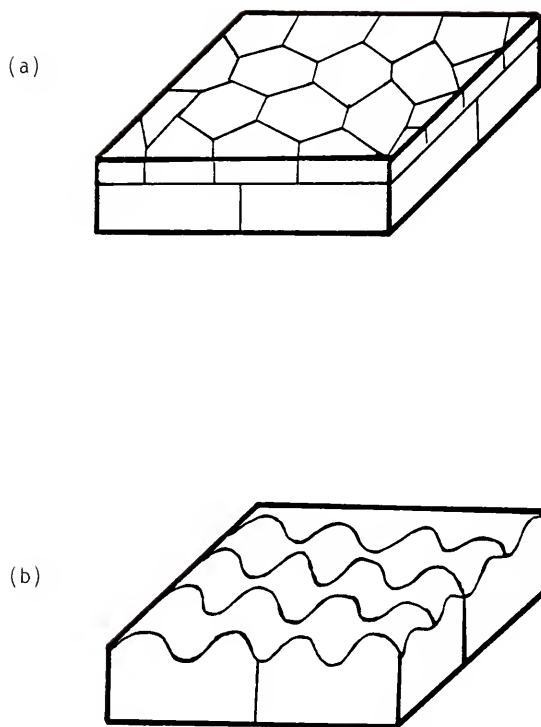


Figure 21. Model Structures to explain the Apparent Difference between the Surface Structure and the Internal Structure : a) Model A , b) Model B

"perturbation," i.e. surface roughness, are identical, the same surface structure may be obtained by SEM for both models. Similarly, large grains as well as small grains may be observed by TEM examination because image formation in TEM is achieved by the diffraction contrast of the transmitted electrons [50].

Thermodynamically, the structure of model A is less likely to occur because it possesses a large amount of grain boundaries although grain boundaries are expected to be eliminated during annealing in order to reduce the total free energy by reducing interfacial energy. Also, knowing that the as deposited In/Au composite films have the columnar structure, in which the grains are extending through the entire film (see Figure 16) the granular structure in model A, in which small grains are embedded on the surface of large grains, is not likely to develop during annealing [82].

On the other hand, the structure of model B is more likely to occur because the as deposited In/Au composite film has a rough surface. The evidence for the existence of model B structure, however, was achieved by XTEM examination of In/Au composite films annealed at 400 C and 500 C. Figure 22 illustrates the cross section of the In/Au composite film annealed at 400 C in which some large grains of about 2000 Å in diameter and some surface roughness whose sinusoidal "perturbation" wavelength and amplitude are 750 Å and 100 Å, respectively, are clearly seen. Several small grains near the surface may be attributed to columnar grains whose grain boundaries are located under some angle with respect to substrate surface normal so that only a section of the large grain is seen in the projected image of the

cross section of the film. A similar grain size and surface roughness in the sample annealed at 500 C are shown in Figure 23.

In summary, the origin of the apparent difference between surface structure and internal grain structure is believed to be due to the surface roughness of In/Au films annealed in air.

c) Texture

X-ray diffraction patterns for annealed In/Au composite films are shown in Figure 24. All the possible diffractions of gold, namely {111}, {200}, {220}, {311} and {222} peaks, are observed. The relative intensity of each peak with respect to the intensity of the {111} peak is tabulated in Table 4. By comparing these relative intensities with those of gold powders as listed in JCPDS, a relatively random orientation of the grains was found. Little change in the relative intensities with annealing temperature increase was found. This suggests that no significant preferential grain growth along certain crystallographic directions during annealing occurred.

d) Distribution of In and phase formation during annealing

When In/Au composite films are annealed in air, interdiffusion of the components is likely to occur. Indium will be redistributed to form a solid solution, intermetallic compounds, or oxides depending upon the annealing conditions. Identification of the phases formed and their locations in the film is essential to the understanding of the microstructural evolution during annealing.

The equilibrium binary phase diagram for the Au-In system (Figure 25) shows at least 6 intermetallic compounds [83-85], e.g.



Figure 22. Cross Sectional Transmission Electron Micrograph of In/Au Composite Films Annealed at 400 C in Air



Figure 23. Cross Sectional Transmission Electron Micrograph of In/Au Composite Films Annealed at 500 C in Air

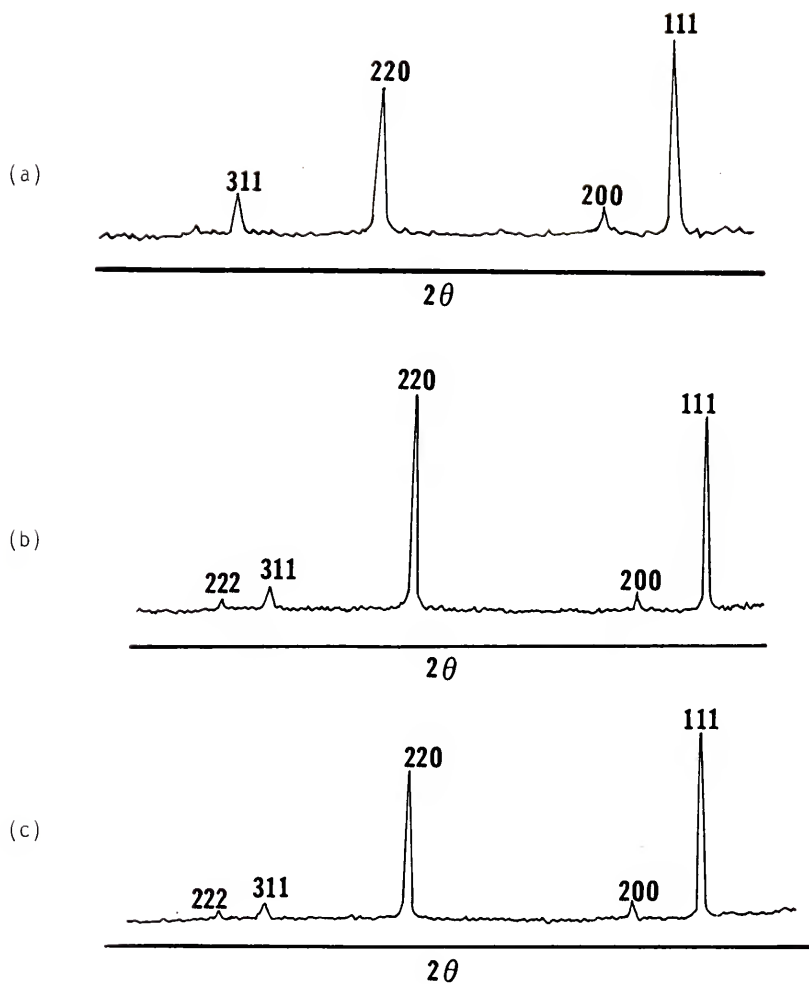


Figure 24. X-Ray Diffraction Patterns of In/Au Composite Films
Annealed in Air at : a) 300 C, b) 400 C, c) 500 C

Table 4. Values of I_{hkl}/I_{111} for In/Au Composite Films Annealed at Various Temperatures in Air, As Measured by X-Ray Diffraction

	$I_{hkl}/I_{111}, \%$			
	In/Au Composite			
	Au Powder	300 C	400 C	500 C
111	100	100	100	100
200	52	30	14	13
220	32	80	100	72
311	36	40	16	18
222	12	6	11	8

Au-In Gold-Indium

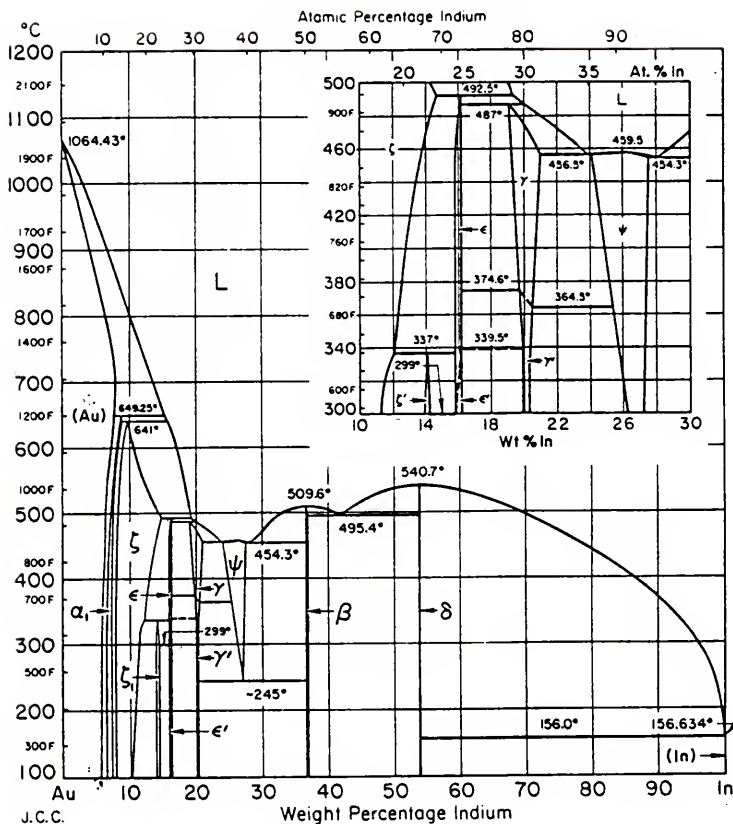


Figure 25. Equilibrium Binary Phase Diagram for Au-In System

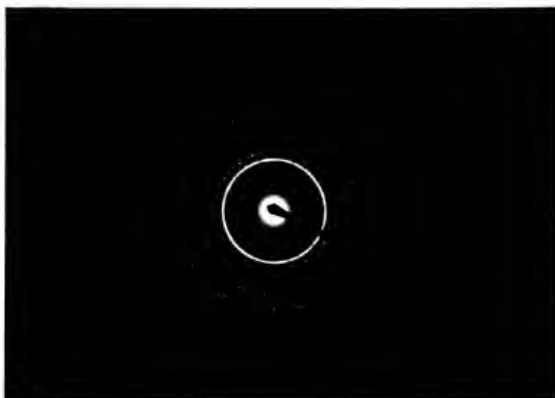
Au_7In , Au_4In , Au_3In , Au_9In_4 , AuIn and AuIn_2 . The solid solubilities of indium in gold at 500 C and at room temperature are reported to be about 10 at. % and 7 at. %, respectively. No solid solubility of gold in indium is reported.

In addition to the intermetallic compounds, three different indium oxides, which are stable in the temperature ranges in which the experiments were conducted, are expected to occur [86]. These oxides are InO , In_2O and In_2O_3 .

The amount of indium in the present In/Au composite films is less than 5 at. %, assuming that all the indium would diffuse into the gold without any chemical reaction. This may suggest that indium is distributed in gold as a solid solution. However, since the structure of In/Au composite films consists of a 100% gold film immediately on top of a 100% indium underlay, any phases mentioned above may be formed depending upon the annealing conditions such as annealing time, temperature, and atmospheres. The identification, the distribution and the characterization of the phase or phases formed during annealing have been accomplished with the combinational use of TEM, AES and XTEM with EDX techniques.

All In/Au composite films annealed in air revealed the same additional diffraction rings in SAD patterns as shown in Figure 26. Based upon the structural informations of the intermetallic compounds and oxides available in the literature and in the JCPDS data, the phase which produces the observed rings is identified as In_2O_3 . The orientation of In_2O_3 crystals corresponding to each diffraction ring is

(a)



(b)



(c)

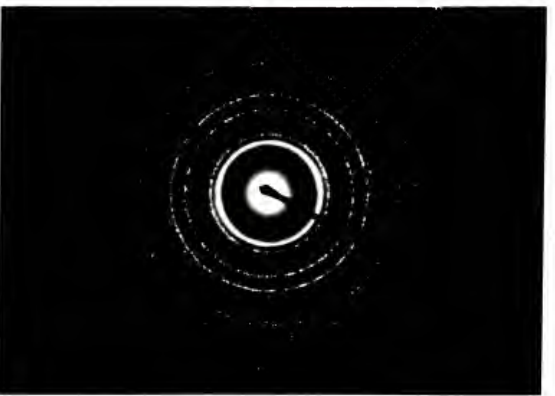


Figure 26. SAD Patterns of In/Au Composite Films Annealed in Air at : a) 300 C, b) 400 C, c) 500 C

also shown in Figure 27. The sharp ring patterns suggest that In_2O_3 has a fine-grained, polycrystalline structure.

The distributions of indium in In/Au composite films after annealing as monitored by AES sputter profiling are shown in Figure 28. High concentrations of In and O on the surface were observed in all cases (300 C, 400 C and 500 C), which indicates the formation of an indium oxide layer on the surface. This suggests that most of the indium did diffuse from the underlay through gold film to the free surface. The thickness of the oxide on the free surface was found to grow as the annealing temperature increased as shown in Figure 29. The thickness was measured by the sputter time required to reduce the indium signal to 50%. In order that indium oxide can grow in excess of a monolayer, the diffusion of either the oxygen or indium through the oxide layer, or both is required. This will depend on the ease of diffusion of the species through the oxide in a given annealing condition [87]. We note that the diffusion rates are temperature dependent following an Arrhenius form. Thus, the thickness increase with increasing annealing temperature is believed to be associated with a higher diffusivity of indium or oxygen through the oxide layer at higher temperatures.

The physical dimensions of the In_2O_3 grains on the surface were studied by XTEM examination of the In/Au films annealed at 400 C as shown in Figure 30. We observe a fine-grained oxide layer, whose mean grain diameter and thickness are about 200 Å and 100 Å, respectively. To further investigate the indium oxide layer on the surface, an EDX analysis was carried out using the STEM mode at two different locations

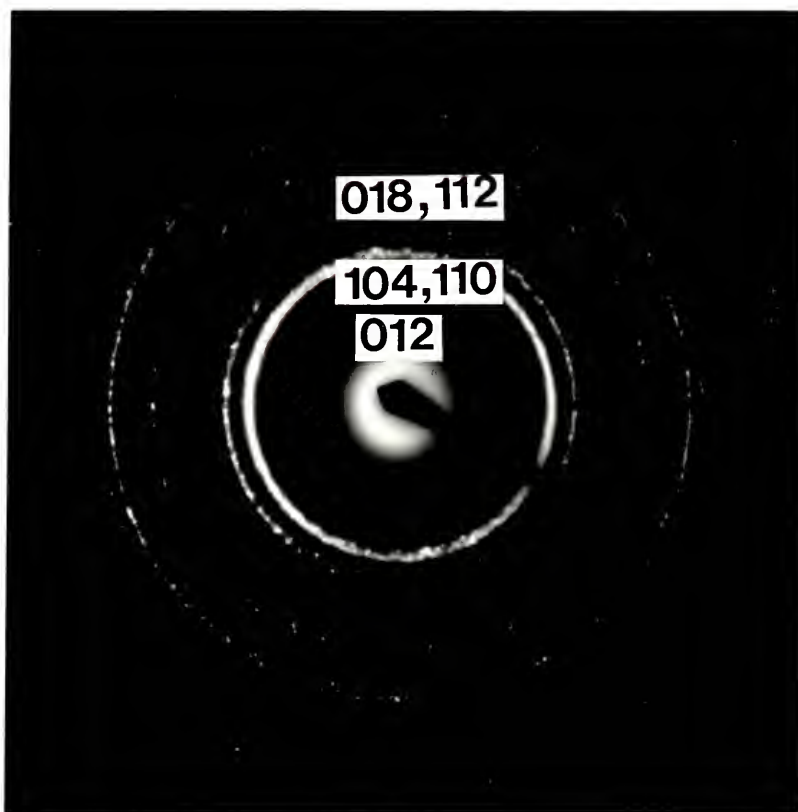


Figure 27. In_2O_3 Phase Identified in SAD Patterns of In/Au Composite Films Annealed in Air

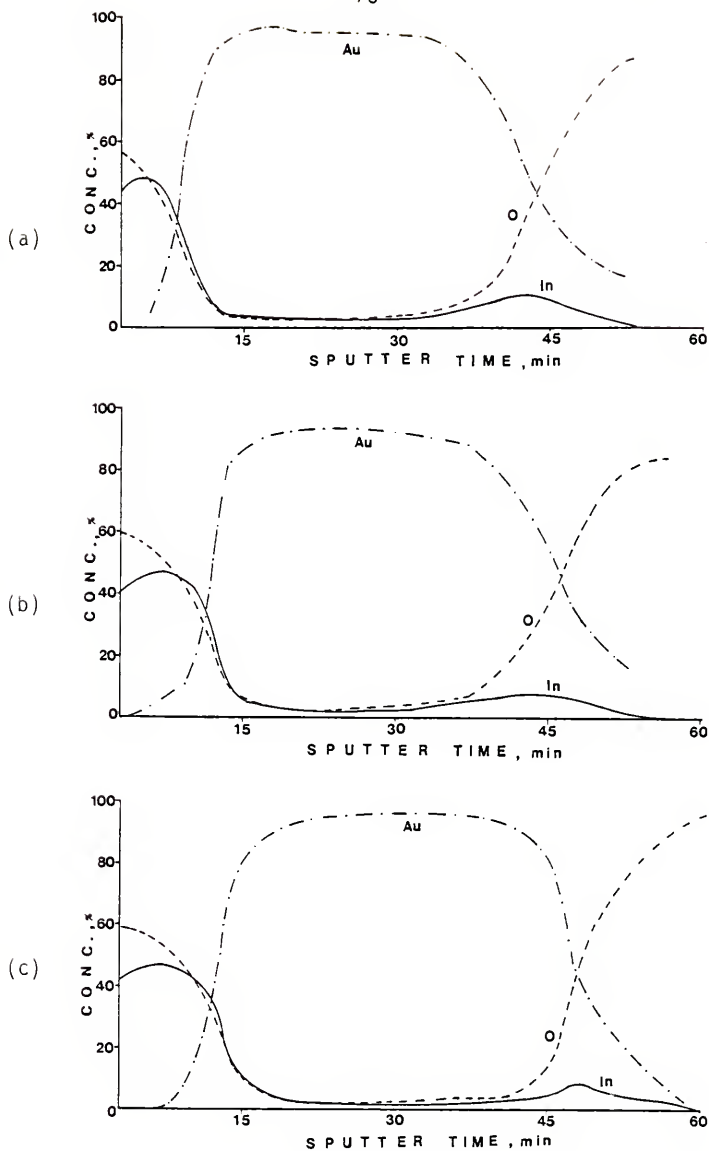


Figure 28. AES Sputter Profiles of In/Au Composite Films Annealed in Air at : a) 300 C, b) 400 C, c) 500 C

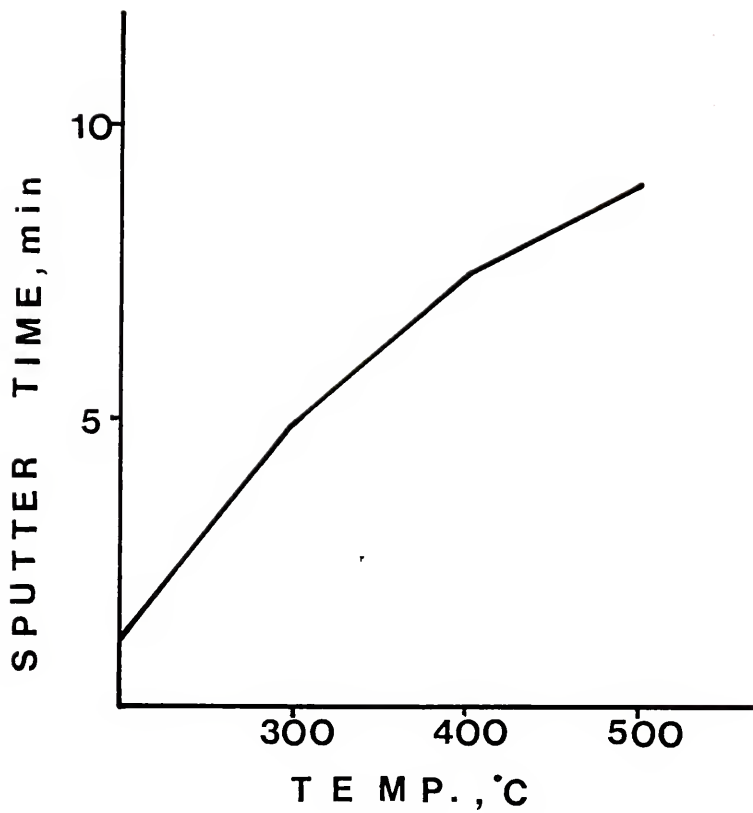


Figure 29. Thicknesses of Surface Indium Oxide in In/Au Composite Films Annealed in Air measured from AES Sputter Profiles

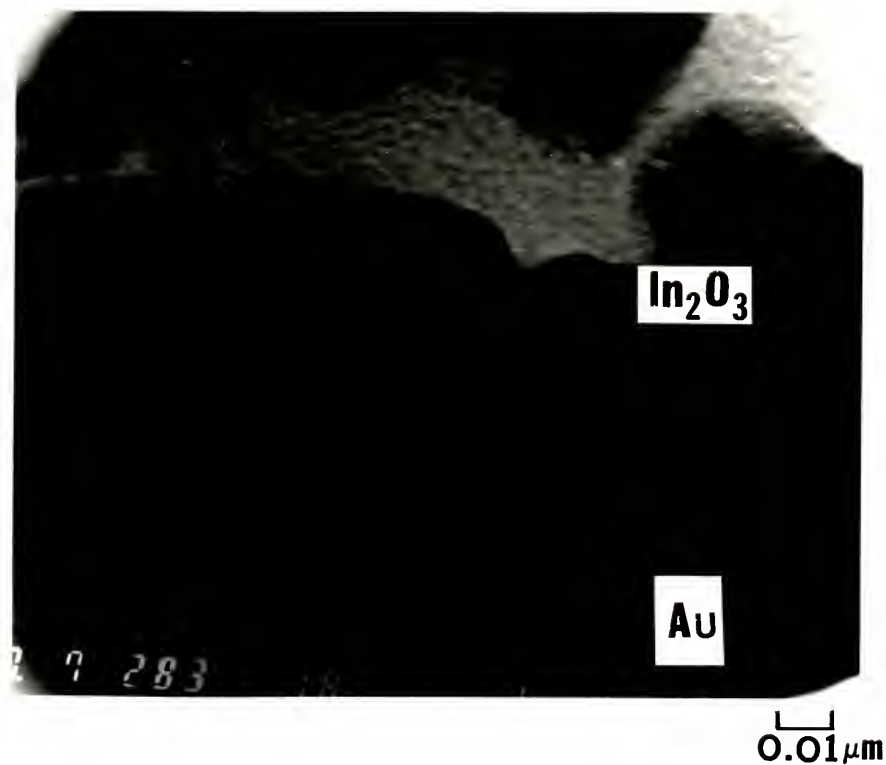


Figure 30. Cross Sectional Transmission Electron Micrograph of In/Au Composite Films Annealed at 400 C in Air showing Indium Oxide at the Free Surface

in the film, i.e., the surface region and the middle region of the gold grain. The beam size of the probe was less than 20 Å in diameter. The analysis showed that the intensity of indium signal (at 3.29 KeV) which is obtained from the surface region (Figure 31a) was about 50% higher than that from the middle region of a gold grain (Figure 31b). This again suggests the presence of indium oxide on the surface.

We attempt now to estimate the thickness of the oxide layer. The maximum thickness of In_2O_3 which is theoretically possible when all indium from the underlay of 100 Å thickness diffuses to the surface and forms In_2O_3 is calculated as follows.

Let t_{in} = thickness of indium, t_{ox} = thickness of In_2O_3 , d_{in} = density of indium, d_{ox} = density of In_2O_3 , M_{in} = molecular weight of indium, M_{ox} = molecular weight of In_2O_3 , A = unit area, N_{in} = number of moles of indium and N_{ox} = the number of moles of In_2O_3 . The density of indium can be written

$$d_{\text{in}} = M_{\text{in}} \times N_{\text{in}} / A \times t_{\text{in}}$$

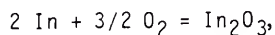
Rearranging,

$$N_{\text{in}} = d_{\text{in}} \times A \times t_{\text{in}} / M_{\text{in}}$$

Similarly, the density of the indium oxide can be used to write

$$N_{\text{ox}} = d_{\text{ox}} \times A \times t_{\text{ox}} / M_{\text{ox}}$$

From the reaction



$$N_{in} = 2 N_{ox}$$

Inserting the values available in the literature [86,88], the thickness of indium oxide is obtained by

$$\begin{aligned} t_{ox} &= 1/2 (d_{in}/d_{ox}) (M_{ox}/M_{in}) \times t_{in} \\ &= 120 \text{ \AA}. \end{aligned}$$

The maximum thickness of In_2O_3 on the surface from a 100 \AA indium underlay is thus about 120 \AA. The experimentally observed thickness, which is about 100 \AA (Figure 30), is in reasonable agreement with the result of this calculation. We need to note that our AES sputter profile data also showed small amounts of indium (and oxygen) in the gold film. If we consider some indium oxide left behind in the film, the agreement between calculation and experiment becomes even more reasonable.

The location of indium oxide in the film was difficult to see in electro-optical micrographs because of the small amounts involved. However, in one case, a grain boundary as shown in Figure 32 revealed nearly the same contrast as the surface oxide, which might suggest that indium oxide in the film is located along some grain boundaries. Further confirmation of indium enrichment along the grain boundaries with EDX analysis was not possible because the area of interest was usually too small for a reasonable analysis.

. In summary, by utilizing the combination of TEM, XTEM with EDX and AES techniques, the formation of polycrystalline In_2O_3 with a thickness

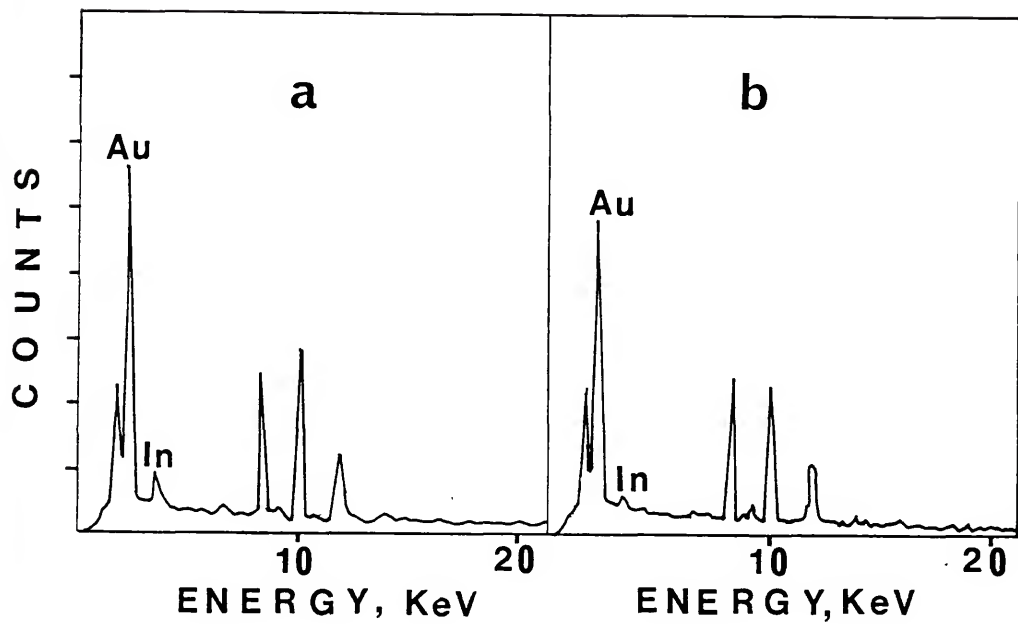


Figure 31. EDX Analysis of In/Au Composite Films Annealed in Air from Two Different Locations in the Film :
a) surface region, b) middle region

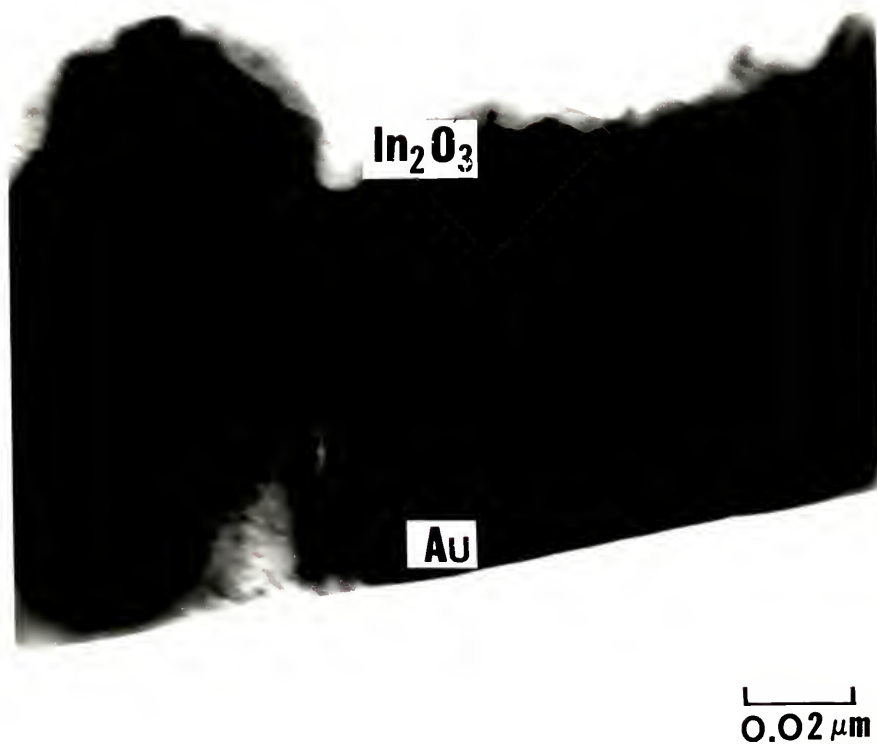


Figure 32. Cross Sectional Transmission Electron Micrograph of In/Au Composite Films Annealed at 400 C in Air showing Indium Oxide along the Grain Boundary

and mean grain diameter of about 100 Å and 200 Å, respectively, has been observed for In/Au composite films annealed in air.

4.2.3. In/Au Composite Films Annealed in Hydrogen

a) Grain structure

The grain structures of In/Au composite films annealed at 300 °C, 400 °C and 500 °C in H₂ examined by TEM are shown in Figure 33. A drastic increase in grain diameter with annealing is observed. The change in the mean grain diameter as a function of the annealing temperature is shown in Figure 34. The error bars indicate as usual the standard deviation. The most significant grain growth was observed in the sample annealed at 500 °C, where very large grains with diameters greater than 1 µm were easily distinguished. This substantial grain growth accompanied by a wide grain size distribution may result from the preferential grain growth along certain crystallographic orientations, presumably (111) parallel to the substrate surface. As these grains grow preferentially, other grains shrink in size and a wider grain size distribution may result.

b) Surface morphology

SEM micrographs for In/Au composite films annealed at 300 °C and 400 °C in H₂ revealed very little structural changes of the surfaces (Figure 35). The films annealed at 500 °C will be discussed separately below. In these films, the surface morphology of the as deposited In/Au composite films seemed to be preserved; that is no significant grain growth and grain boundary grooves were observed. We know from

(a)



(b)


0.2 μm

(c)



Figure 33. Transmission Electron Micrographs of In/Au Composite Films Annealed in H_2 at : a) 300 C, b) 400 C, c) 500 C

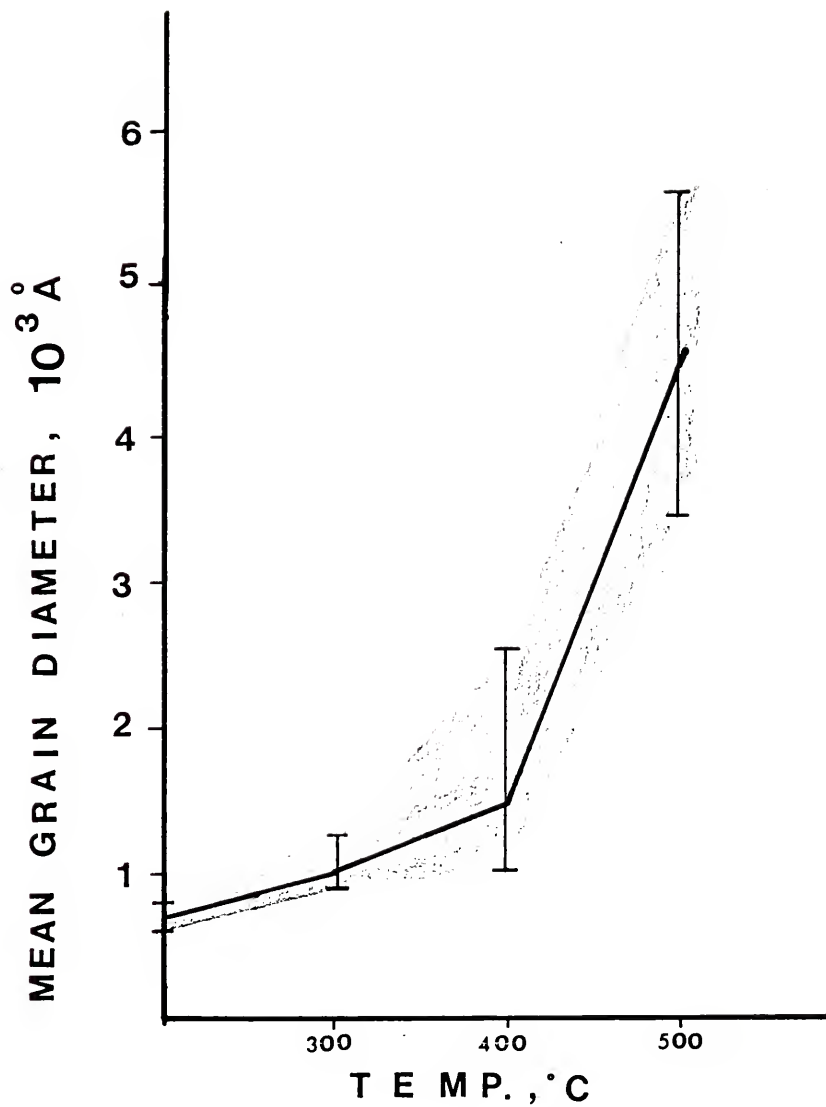
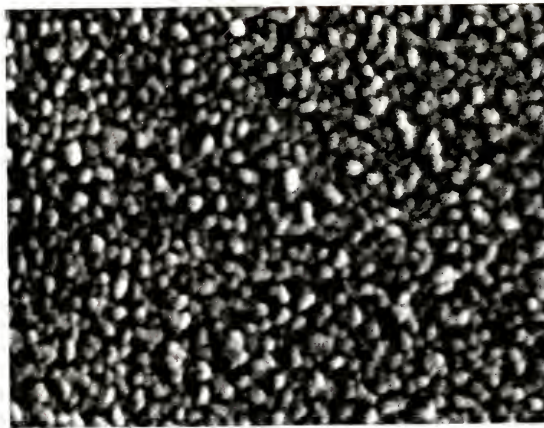


Figure 34. Mean Grain Diameters measured from Transmission Electron Micrographs of In/Au Composite Films Annealed at Various Temperatures in H_2

(a)

0.2 μm

(b)

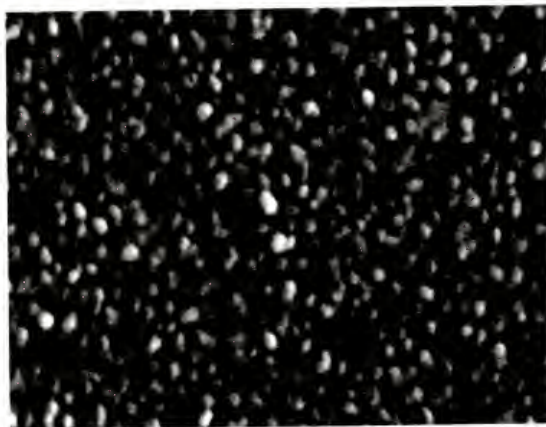


Figure 35. Scanning Electron Micrographs of In/Au Composite Films Annealed in H_2 at : a) 300 C, b) 400 C, c) 500 C

the results reported above that the significant grain growth which occurred during annealing can be observed mainly by TEM. The difference between the surface structure and the internal grain structure is again noticed. This apparent discrepancy is believed to be result of the surface roughness of these samples. Indeed, for an In/Au composite film annealed at 400 C, the bright field and the dark field cross sectional TEM micrographs shown in Figure 36a and Figure 36b reveal large grains of about 3000 Å in diameter and a rough surface whose sinusoidal "perturbation" wavelength is about 750 Å. Therefore, the fine surface structure observed by SEM is believed to be caused by surface roughness, as before, rather than by real grain structure.

A substantially different surface morphology was observed when In/Au films were annealed at 500 C in H_2 . The SEM micrograph (Figure 37) shows a very coarse-grained structure and some severe grain boundary grooves at the grain boundary vertices. The cross sectional TEM micrographs (Figure 38) reveal very large grains whose diameter is greater than 7500 Å and an extremely smooth surface. This suggests that the surface roughness has been relaxed during annealing.

The flattening of the rough surface and the evolution of grain boundary grooves are both caused by the capillary-induced mass transport during annealing [25-27,89-91]. The mass transport, either by volume diffusion, surface diffusion or evaporation-condensation mechanisms, is a thermally activated process and therefore temperature dependent. Depending on the annealing conditions, the mass transport and the subsequent flattening or thermal grooving may not occur due to the kinetic limit. Apparently, annealing at 300 C and 400 C for 1 hr in H_2

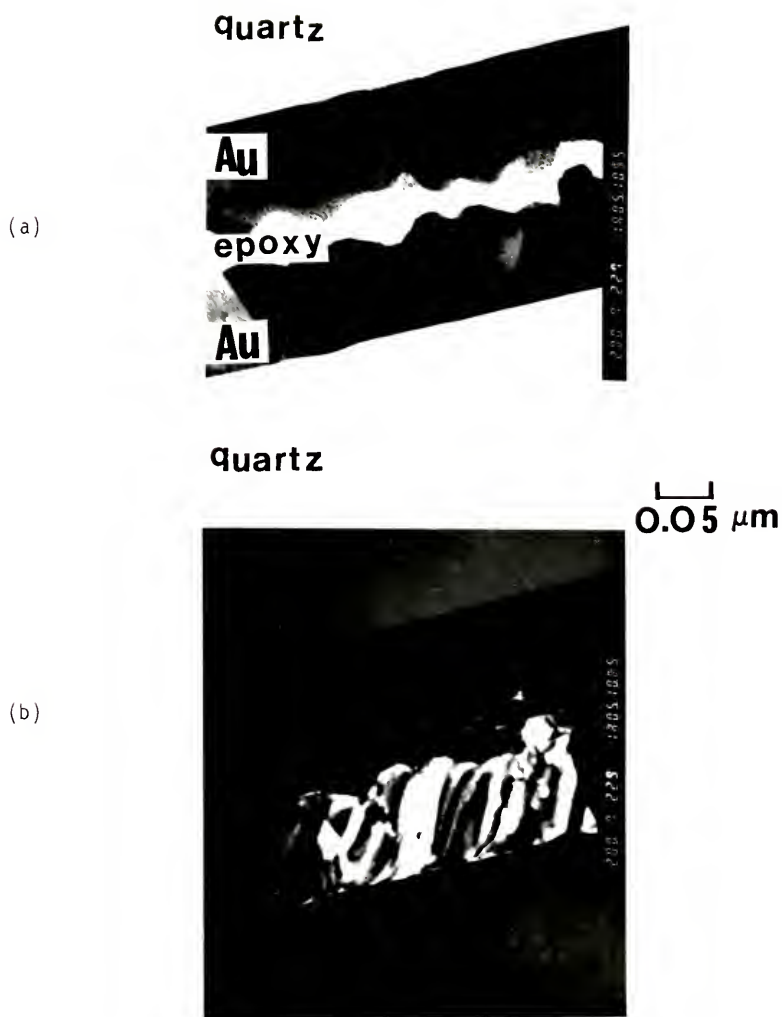


Figure 36. Cross Sectional Transmission Electron Micrographs of In/Au Composite Films Annealed at 400 C in H_2 :
 a) bright field image, b) dark field image




0.2 μm

Figure 37. Scanning Electron Micrograph of In/Au Composite
Films Annealed at 500 C in H_2

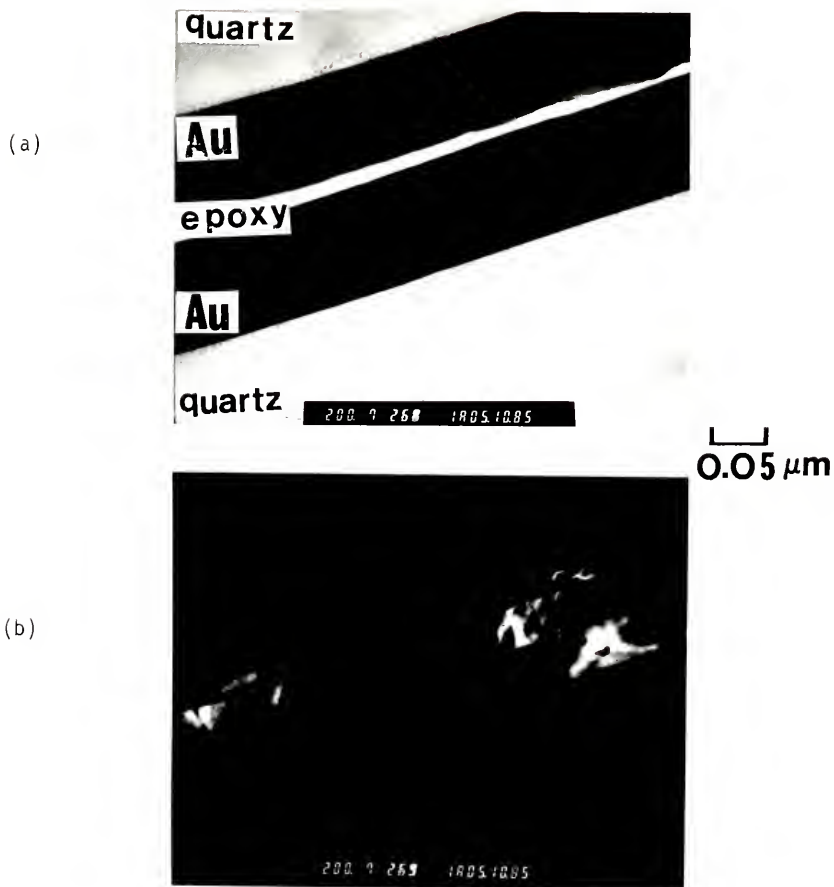


Figure 38. Cross Sectional Transmission Electron Micrographs of In/Au Composite Films Annealed at 500 C in H_2 :
 a) bright field image, b) dark field image

did not provide the conditions to activate the mass transport so that the relaxation of the roughness has not occurred during annealing. On the other hand, annealing at 500 C for 1 hr in H_2 did provide the conditions to allow the flattening and the grain boundary grooving to occur.

c) Texture

X-ray diffraction patterns for In/Au films annealed at 300 C, 400 C and 500 C are shown in Figure 39. The relative intensity of each diffraction peak with respect to the intensity of the $\{111\}$ peak is listed in Table 5. In/Au composite films annealed at 300 C and 400 C revealed a relatively random orientation; that is they displayed all diffraction peaks (Figure 39a and Figure 39b). However, the In/Au composite film which was annealed at 500 C revealed only $\{111\}$ and $\{222\}$ diffraction peaks, which suggested a (111) texture parallel to the substrate surface (Figure 39c).

SAD patterns complement this information. In/Au composite films annealed at 300 C and 400 C in H_2 revealed that the $\{111\}$ diffraction ring was the most intensive one (Figure 40a and 40b). This suggests the random orientation of the grains in the film. However, the In/Au composite film annealed at 500 C revealed that the $\{220\}$ ring was more intensive than the $\{111\}$ ring and also showed some directionality as well (Figure 40c), which suggests a (111) texture parallel to the substrate surface.

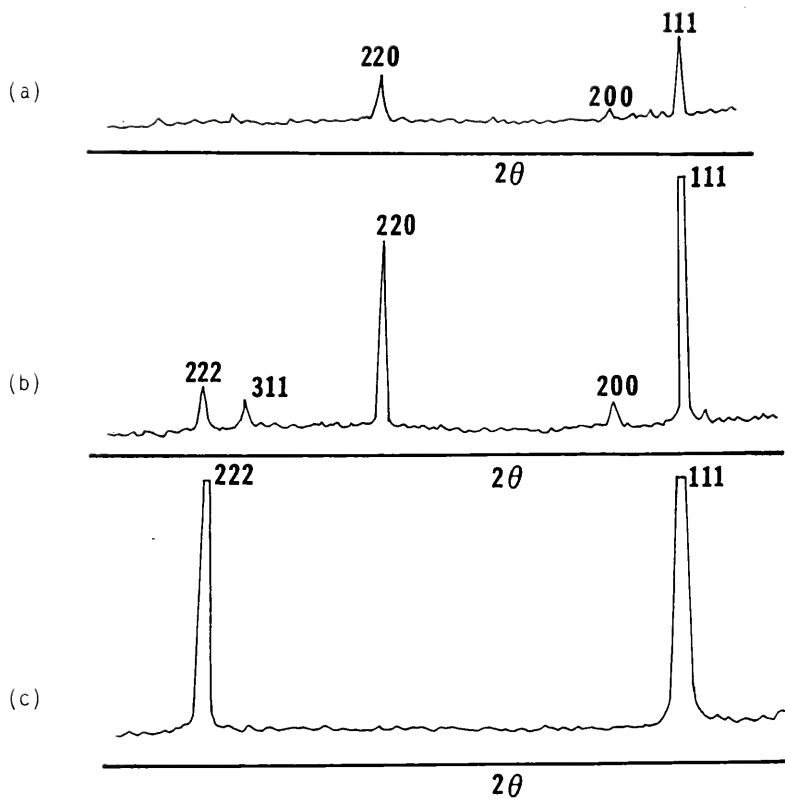
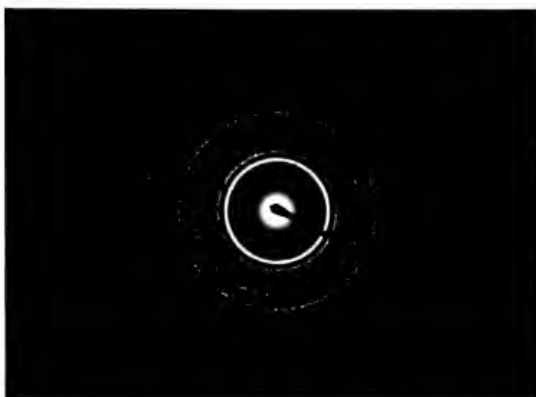


Figure 39. X-Ray Diffraction Patterns of In/Au Composite Films Annealed in H_2 at : a) 300 C, b) 400 C, c) 500 C

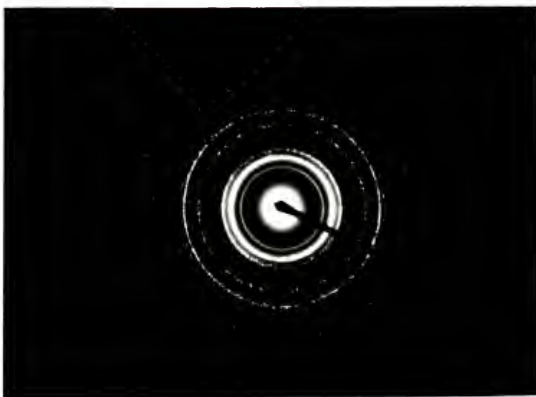
Table 5. Values of I_{hkl}/I_{111} for In/Au Composite Films Annealed at Various Temperatures in H_2 , As Measured by X-Ray Diffraction

	$I_{hkl}/I_{111}, \%$			
	Au Powder	In/Au Composite		
		300 C	400 C	500 C
111	100	100	100	100
200	52	20	4	0
220	32	64	26	0
311	36	22	5	0
222	12	5	7	5

(a)



(b)



(c)



Figure 40. SAD Patterns of In/Au Composite Films Annealed in H_2 at : a) 300 C, b) 400 C, c) 500 C

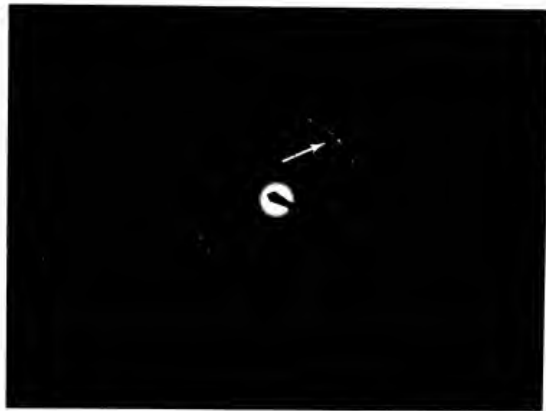
d) Distribution of indium and phase formation during annealing

Figure 41a shows an SAD pattern which was obtained from an In/AU composite film annealed at 400 C in H_2 . We notice an additional diffraction ring in SAD patterns whose diameter is 28 mm when the camera length is 137 cm. The spot pattern which was taken from this specimen of a large grain using a small SAD aperture is shown in Figure 41b. A hexagonal symmetry of the extra spots along with the $\{111\}$ diffraction spots is shown. Both ring and spot patterns give the interplanar spacing of 2.49 Å. This new pattern was confirmed by x-ray diffraction at $2\theta = 34$ degrees which was measured at the fixed angle for an extended counting time.

In order to identify the phase which is responsible for the additional diffraction, structural information for pure indium, intermetallic compounds and indium oxides were consulted. None of these phases met exactly the observed interplanar spacing and the observed Bragg angle. The closest candidate among the intermetallic compounds which would contain this pattern is Au_7In [92,93]. However, if this would be the right phase, other diffraction rings whose intensities are higher should have been observed as well. This has not been observed, which excludes the possibility of Au_7In .

It is believed that this "anomalous" diffraction is caused by a "forbidden" diffraction of gold. Yacaman et al. has indeed reported the same diffraction pattern for vapor deposited gold films [94]. They showed that the "anomalous" diffraction pattern results from $1/3 \langle 422 \rangle$ reflections of HCP gold. Various physical reasons to cause HCP structure in a gold film have been discussed in the literature [95-98].

(a)



(b)



Figure 41. SAD Patterns of In/Au Composite Films Annealed at 400 C in H_2 showing some Extra Diffraction Patterns :
a) ring patterns, b) spot patterns

Among them, some form of surface roughness such as kinks, steps and supersaturated vacancies are believed to be most probable sources. As a matter of fact, the In/Au composite films annealed at 300 C and 400 C are known to have a very rough surfaces as shown above. Furthermore, the fact that the "anomalous" diffraction ring was not seen in the specimens annealed at 500 C, which has a flat surface may add to the evidence that surface roughness is responsible for the anomalous diffraction in gold films.

The distribution of indium in In/Au composite annealed in H_2 as monitored by AES sputter profiling is shown in Figure 42. A considerable concentration of indium as well as some oxygen is observed on the surface. This again suggests the formation of indium oxide on the surface. However, the thickness of the oxide is much less than that of the same films annealed in air. The oxygen signal dropped very rapidly to almost zero as the sputtering started. Only indium was observed later on in the gold film.

The indium oxide on the surface is believed to result from atmospheric exposure of the specimens during transfer from the annealing furnace to the AES chamber. This can be deduced from the observation that the thickness of the surface oxide is almost the same for all annealing temperatures, as shown in Figure 43. This suggests that the oxidation did not take place during annealing in H_2 . A small calculation involving the partial pressure of oxygen needed to oxidize the film in air and in H_2 has been made to support this suggestion.

From the thermodynamic data reported by Samsonov [86], the standard free energy formation of In_2O_3 can be plotted on the

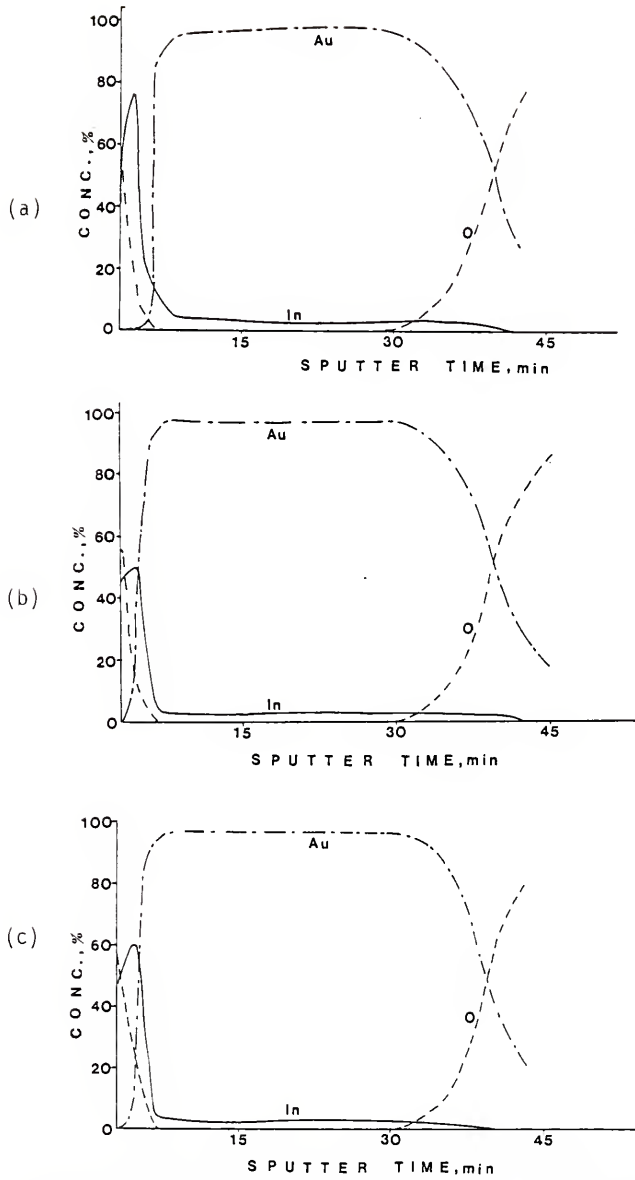


Figure 42. AES Sputter Profiles of In/Au Composite Films Annealed in H_2 at : a) 300 C, b) 400 C, c) 500 C

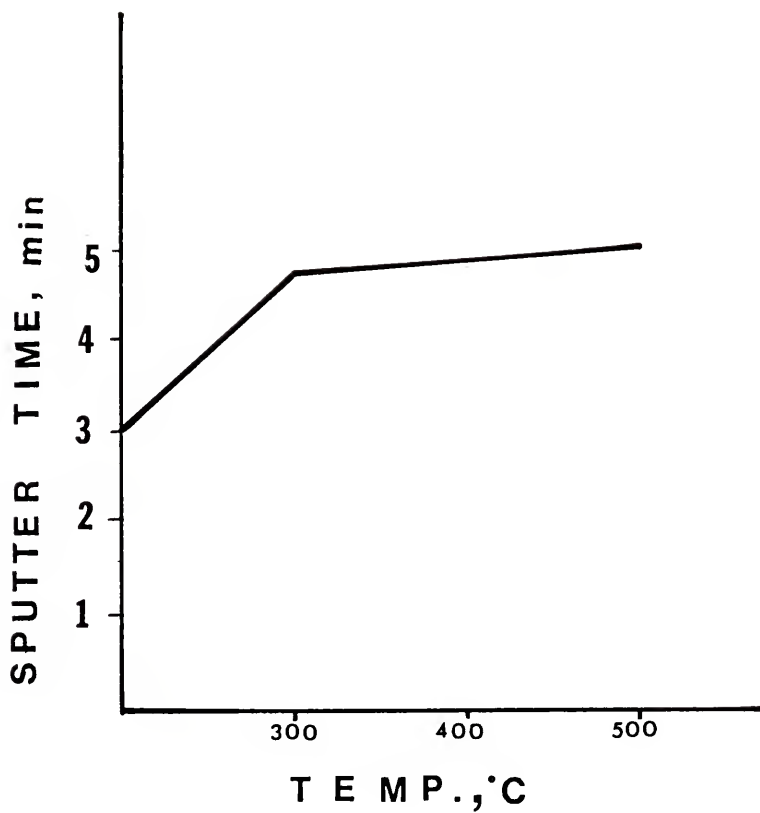


Figure 43. Thicknesses of Surface Indium Oxide in In/Au Composite Films Annealed in H_2 measured by AES Sputter Profiles

Richardson's diagram as shown in Figure 44 [99]. It is shown that indium oxidizes in an atmosphere in which the partial pressure of oxygen is larger than 10^{-90} atmosphere at room temperature. This suggests that we can not prevent the oxidation of indium at room temperature. Furthermore, in order to check any kinetic limit for oxidation, the impingement rate of oxygen molecules in air at room temperature is calculated [100]. Assuming ideal gas kinetics, the impingement rate calculated is about 5×10^{22} molecules/cm²-sec. Assuming the surface atom density of indium is 10^{15} atoms/cm², then 10^7 monolayers of oxygen molecules/sec will strike the surface. This is more than sufficient to allow the oxide growth.

In contrast to this, oxidation in hydrogen atmosphere at the temperatures above 300 C will take place if the H_2/H_2O ratio is smaller than 10^4 . The H_2 used in the experiment contained less than 10 ppm H_2O resulting in a H_2/H_2O ratio in H_2 of greater than 10^5 . Thus, no oxidation should have taken place during annealing in H_2 . Instead, a reduction should have occurred.

In summary, no intermetallic compounds and no oxides were formed during annealing of In/Au films in H_2 . The uniform concentration of indium in the gold film down to the substrate surface suggests the formation of a solid solution of indium in gold. The amount of indium was calculated to be less than 5 at. % which is less than the solubility at room temperature. Therefore, indium in the In/Au composite film is distributed uniformly as a solute in the gold film when it is annealed in H_2 atmosphere.

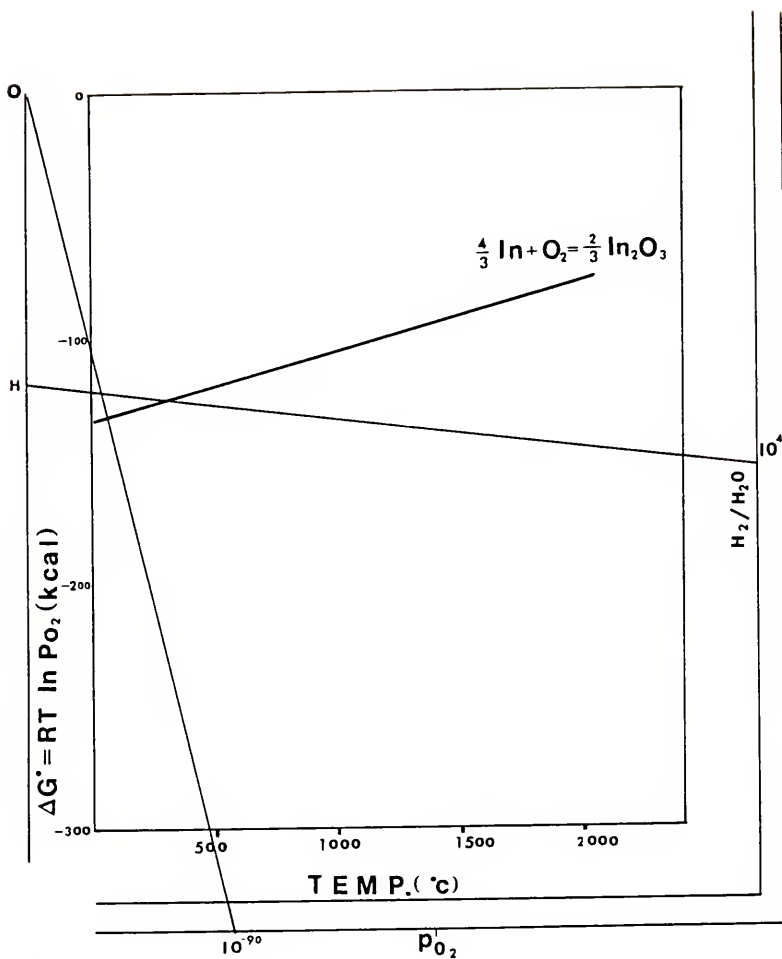


Figure 44. Standard Free Energy of Formation of Indium Oxide as a Function of Temperature

4.3. Effects of In and In₂O₃ on the Microstructural Evolutions

4.3.1. Effects of In on the Microstructure of Au Films During Deposition

The effects of indium underlays upon the microstructural evolution of gold films during deposition can be determined by comparing the microstructure of the as deposited pure Au film with that of the as deposited In/Au composite film. The characteristics of the microstructure of these two types of films are summarized in Table 6.

The differences in the microstructure are evident. While the pure Au films have a mixture of a fine-grained and coarse-grained structure with a (111) texture parallel to the substrate surface and a smooth surface, the In/Au composite films have a uniform, fine-grained structure with a random orientation and a rough surface. The microstructure of pure Au films is believed to result from the preferred nucleation and/or growth during deposition which is governed by the smoothness of the substrate and the high kinetic energy of the evaporated gold atoms. The microstructure of gold in In/Au composite films is mainly affected by the microstructure of the indium underlay which has a fine-grained structure and a rough surface.

From these microstructural differences, the following parameters caused by indium underlays upon the microstructure of gold films can be deduced:

- 1) randomization of the grain orientations
- 2) refinement of the grain size
- 3) uniformity of the grain size distribution
- 4) roughening of the surface

Table 6. Characteristics in Microstructures of As Deposited Pure Au Films and As Deposited In/Au Composite Films

	Pure Au	In/Au Composite
Texture	111	Random
Grain Size	1000 Å	700 Å
Size Distribution	Wide	Narrow
Surface Morphology	Smooth	Rough

All these effects are believed to result from the decreased surface mobility of gold adatoms during deposition. The decrease in surface mobility of gold adatoms is associated with the fine-grained structure and the rough surface of the indium underlay in the In/Au composite film.

4.3.2. Effects of In_2O_3 on the Microstructural Evolution of In/Au Composite Films

The foregoing sections have shown that indium in In/Au composite films oxidizes to In_2O_3 during annealing in air. Thus, the effects of indium upon the microstructural evolution during annealing should be better referred to as the effects of In_2O_3 . The effects of In_2O_3 during annealing can be appreciated by comparing the microstructures of In/Au composite films annealed in air with those of annealed pure Au films and In/Au composite films annealed in H_2 , because both, annealed pure Au films and In/Au composite films annealed in H_2 , do not form In_2O_3 during annealing. The characteristics of the microstructures of annealed Au films and In/Au films annealed in air and H_2 are summarized in Table 7. The differences in the microstructures can be expressed in terms of grain growth and surface morphology.

a) Grain growth

The changes in the mean grain diameters of annealed pure Au films and In/Au composite films as a function of annealing temperature are summarized in Figure 45. It can be seen there that the grain growth for pure Au films annealed in air and for In/Au composite film annealed in H_2 is substantially larger than for In/Au composite films annealed

Table 7. Characteristics in Microstructures of Annealed Pure Au Films and Annealed In/Au Composite Films

	Temperature Degrees C	Pure Au	In/Au Annealed in Air	In/Au Annealed in H ₂
Texture	300	111	random	random
	400	111	random	random
	500	111	random	111
Grain Size	300	2500 A	800 A	1000 A
	400	3300 A	950 A	1500 A
	500	4800 A	1500 A	4500 A
Size Distribution	300	wide	narrow	narrow
	400	wide	narrow	narrow
	500	wide	narrow	wide
Surface Morphology	300	smooth	rough	rough
	400	smooth	rough	rough
	500	severe grooving	rough	severe grooving

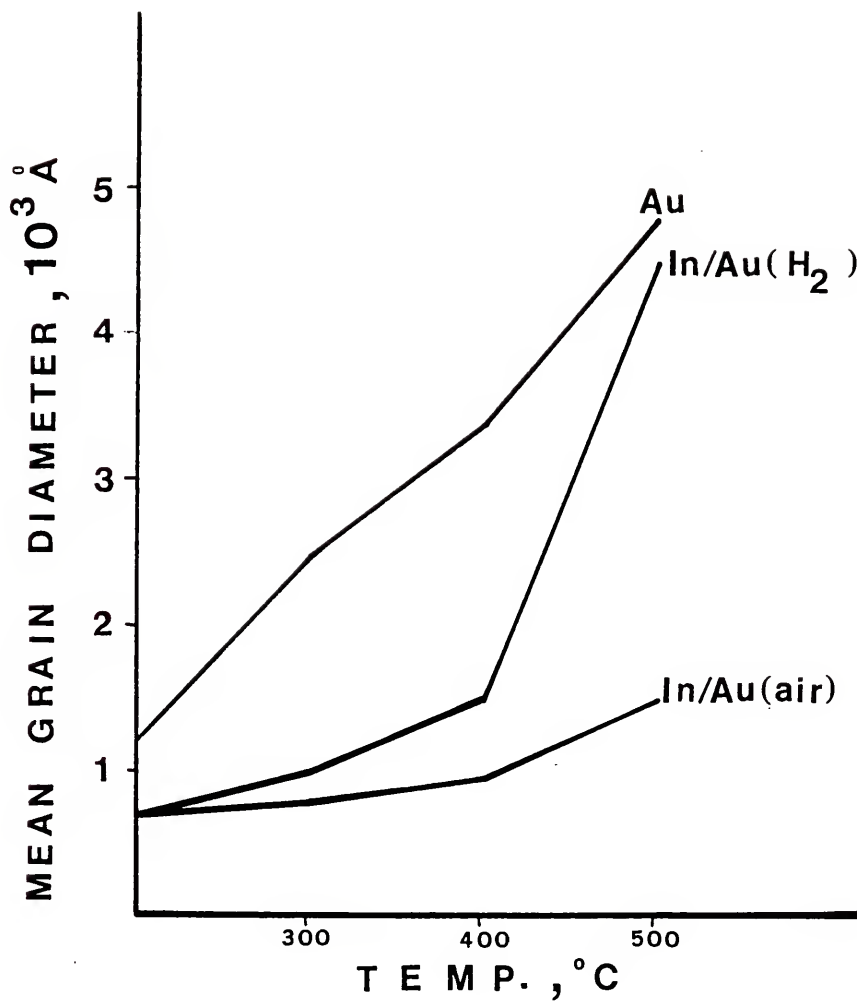


Figure 45. Mean Grain Diameters of Pure Au Films and In/Au Composite Films Annealed at Various Temperatures

in air. The large grain growth for pure Au films is believed to result from the preferential grain growth of the (111) oriented grains during annealing. Our suggestion is based on the observation that the amount of (111) texture increases as the annealing temperature increases. The higher growth rate of the (111) oriented grains during annealing is also believed to be responsible for the large grain growth in the In/Au composite film annealed at 500 C in H_2 , noting that the (111) texture is developed during annealing of the as deposited In/Au composite film which has a fine-grained structure with random orientations.

The In/Au composite films annealed in air show much less grain growth (Figure 45). The cause for this may be traced to the presence of indium oxide. Although the exact location of indium oxide in the gold film is hard to determine because of its small amount, the grain boundaries are considered to be the most probable sites, for the following reasons.

- 1) Most indium atoms diffuse through the grain boundaries of a gold film to form In_2O_3 on the free surface of gold because the grain boundaries act as short circuits for diffusion. That is particularly effective at lower temperatures. If there is some indium left in the gold film during annealing, it is probably distributed near the grain boundaries.

- 2) The uniform concentration of oxygen as well as indium in the gold film as well as indium completely down to the surface of the substrate as revealed in AES sputter profiling analysis suggests that the oxygen has diffused into the Au film during annealing and forms these indium oxide. The diffusion of oxygen, either in ionic form or

as molecules, into these Au films in the temperature range examined here is most likely to occur through the grain boundaries of Au films.

3) Grain boundaries have been known to be the preferred nucleation sites for a new phase because of their higher free energy state due to the interfacial energy [101].

In summary, it is quite likely that indium residing along the grain boundary meets the diffusing oxygen and forms an oxide at or near the grain boundaries. Experimentally, indium oxide along the grain boundary was indeed occasionally observed (Figure 32).

The smaller grain growth in In/Au composite films annealed in air may be explained by the "pinning effect" of indium oxide along the grain boundaries. The retardation of grain boundary migration by the drag, or pinning, imposed on moving interfaces is well understood [102,103]. Drag or pinning may result from impurities, inclusions or precipitates which can form in the matrix or at an interface such as a grain boundary. It is suggested that indium oxide along the grain boundaries inhibits grain boundary migration and subsequent grain growth.

In In/Au composite films annealed in H_2 , indium is assumed to be distributed as a solute in the gold matrix. The effect of the solute on the grain growth kinetics is not clear. It varies markedly from one solute to another in a given solvent [104]. It is, however, worthwhile to emphasize that indium as a solute does not seem to have an retarding effect on the grain growth of In/Au composite films annealed at 500 C in H_2 .

b) Surface morphology

The most significant differences in the surface morphology are shown by comparing pure Au films and In/Au composite films annealed at 500 C as shown in Figure 46. Both pure Au films and In/Au composite films annealed in H_2 reveal smooth surfaces with severe grain boundary grooves at the grain boundary vertices whereas the In/Au composite film annealed in air reveals a rough surface without severe grain boundary grooves.

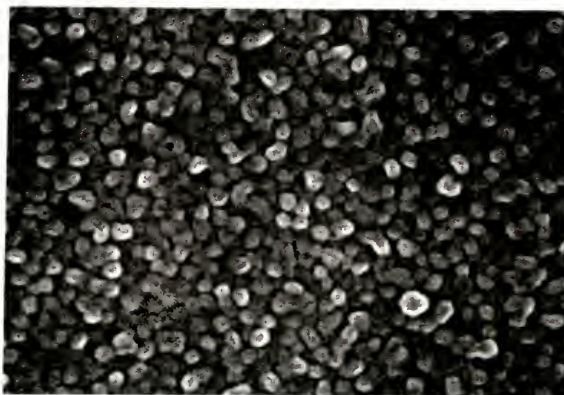
Since as deposited pure Au films have initially very smooth surfaces, the surface morphological changes in annealed Au films must result from the evolution of thermal grooves at the intersection of the grain boundaries and free surfaces. However, since as deposited In/Au composite films originally have rough surfaces, the surface morphological changes in In/Au composite films annealed in H_2 must have contribution from both the grain boundary grooving and the flattening of the rough surface.

The absence of grain boundary grooving and surface flattening in the In/Au composite films annealed in air reveals the beneficial effect of In_2O_3 on the surface for stabilizing the surface structure during heat treatment. The role of In_2O_3 on the gold surface, which causes a stabilization of the surface structure, can be explained by a "capping effect." Both the grain boundary grooving and the flattening of the rough surface are caused by mass transport driven by the surface curvature which is related to the chemical potential. The transport processes that may operate are surface diffusion, volume diffusion, and evaporation-condensation. In the temperature range over which the

(a)



(b)


0.2 μm

(c)



Figure 46. Scanning Electron Micrographs of Annealed Films at 500 C :
a) pure Au films, b) In/Au composite films annealed in Air
c) In/Au composite films annealed in H_2

experiment was conducted, surface diffusion is believed to be the dominant process [26,27]. If the surface of the gold grains are covered, or "capped", with some rigid films such as In_2O_3 , the diffusion of gold atoms along the surface is not so likely to occur.

In order to have any morphological changes on the surface of gold films, morphological changes in the capping layer must also occur. For example, in order to have grooving on the gold grain boundary, the indium oxide layer on the surface must be removed, either by severe grain boundary grooving of the indium oxide or by some loss of adhesion due to stress, so that gold grains and grain boundaries might be exposed to free surface. Thermal grooving of indium oxide is not likely to occur in this temperature range because of the kinetics. Although the surface diffusivity of In_2O_3 is not available from the literature, it seems reasonable to assume that the surface diffusivity of In_2O_3 is much lower than that of gold in the temperature range utilized here because, in general, the diffusivities for the oxides are much lower than those of the metals, especially at lower temperatures. Even if severe grooving of indium oxide occurred somehow, the subsequent grain boundary grooving of gold grains is not likely to occur due to the involvement of additional interfacial energy between gold and the indium oxide.

In addition to the capping effect, thermal stress developed due to the differences in the thermal expansion coefficients of gold and In_2O_3 may also provide an additional effect to reduce the surface morphological changes during annealing [105]. Since gold has a higher thermal expansion coefficient than that of indium oxide, the

compressive stress is expected to be applied to gold during annealing. This compressive stress is believed to prevent the nucleation of cracks and voids on the gold surface which could induce the loss of adhesion. Similar beneficial effects of dielectric overlay coating on the reliability of thin film metallizations by forming a compressive stress has been reported by several investigators [106-111].

CHAPTER 5

CRITICAL CONDITIONS FOR THIN FILM INSTABILITY BY GRAIN BOUNDARY GROOVING

5.1. Derivation of Critical Conditions

The conditions where grain boundary grooves reach the substrate are critical in the stability of thin films because the subsequent hole formation will eventually disconnect the film. These critical conditions, where equilibrium groove depths for a finite grain size are equal to the film thickness, are derived for two cases using a similar approach made by Srolovitz and Safran [46]:

- 1) the groove in the grain boundary where two grains meet, and
- 2) the groove in the grain boundary vertex where three grain boundaries meet.

5.1.1 Grain Boundary

Consider the microstructure in which a thin film is composed of the hexagonal-shaped grains with grain boundaries extending from the free surface to the substrate (Figure 47a). Assume the surface shape of the grain is a spherical cap because it has the minimum surface area. A hexagonal unit cell with a spherical cap is visualized. A cross sectional view of the unit cell is shown in Figure 47b, where B is the cell size, R is the radius of the sphere whose segment forms the

spherical cap of the grain, t and d are the film thickness and the groove depth measured with respect to the top of the spherical cap, respectively and h is the height of the spherical cap with respect to the surface of the flat film. The groove angle is given by

$$\theta = \sin^{-1} (\gamma_g / 2 \gamma_s)$$

where γ_g is the grain boundary energy and γ_s is the surface energy of the grain.

Conservation of film volume requires that the volume of the hexagonal cell of thickness d , V_d , must be same as the volume of the spherical cap, V_s .

Using the relations, $R \sin \theta = B$ and $h = R - R \cos \theta$, V_d and V_s can be written as

$$V_d = \text{area of hexagon} \times \text{thickness} = 2\sqrt{3} B^2 d$$

$$= 2\sqrt{3} R^2 \sin^2 \theta d$$

$$V_s = 1/3 h^2 (3R - h) = 1/3 R^3 (1 - \cos \theta)^2 (2 + \cos \theta).$$

Letting $V_d = V_s$ and rearranging yields an expression for the equilibrium groove depth, d , e.g.,

$$d = 0.3 B (2 - 3 \cos \theta + \cos^3 \theta) / \sin^3 \theta.$$

When the thickness of the film is less than the groove depth, the groove will reach the substrate and the film will be discontinuous in the vertical direction. The critical ratio of the grain size to the

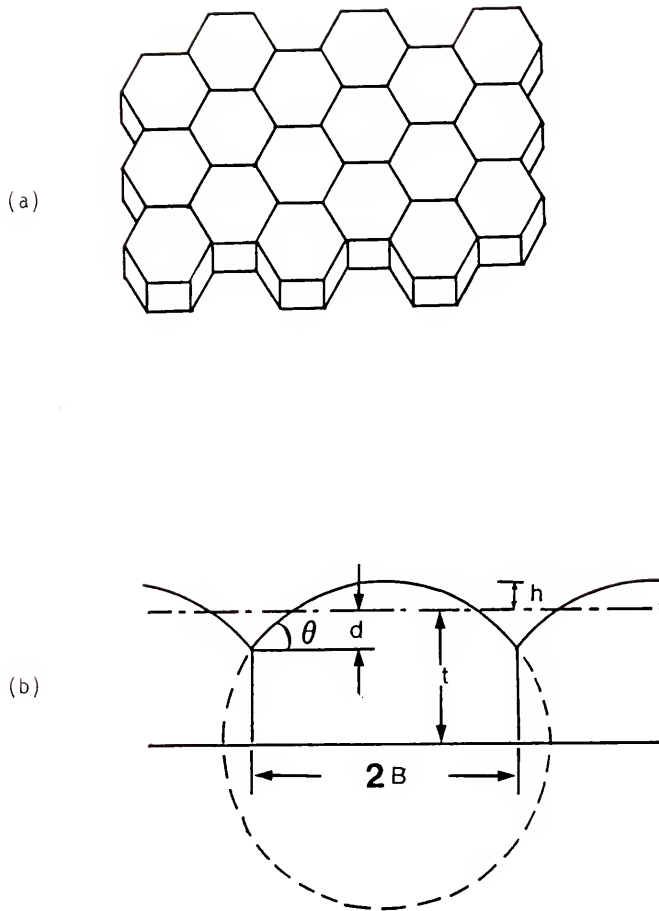


Figure 47. Unit Cell Structure used for Derivation of Critical Ratio for the Grooves in the Grain Boundaries :
 a) a symmetric arrangement of grains in the film
 b) cross sectional view of the unit cell

film thickness below which the groove will reach the substrate is obtained:

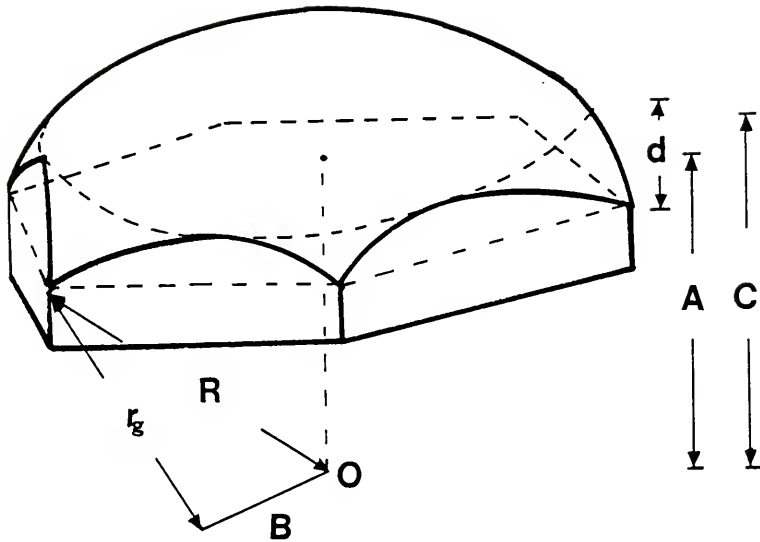
$$(t/B) < 0.3 (2 - 3 \cos\theta + \cos^3\theta)/\sin^3\theta.$$

5.1.2. Grain Boundary Vertex

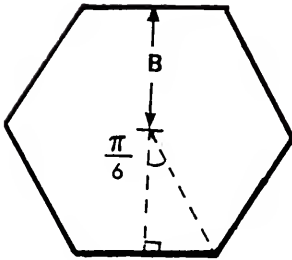
The unit cell structure for calculating the equilibrium depth in the grain boundary vertex is shown in Figure 48a. The grooves in the grain boundaries and the grain boundary vertices appear at the edges and the corners of the hexagonal unit cell with a spherical cap.

In Figure 48a, C is the center of the sphere with radius R whose segment forms the spherical cap, B is the cell size, r_g is the radius of the circle which provides the groove profile in the grain boundary, A and C are the height of groove tips in the grain boundary and the height in the grain boundary vertex with respect to the origin of the sphere, respectively, d is the depth of the groove in the vertex with respect to the surface of the flat film and h is the height of the spherical cap with respect to top of the groove profile in the grain boundary. The top and the front views of the unit cell are shown in Figure 48b and Figure 48c, respectively.

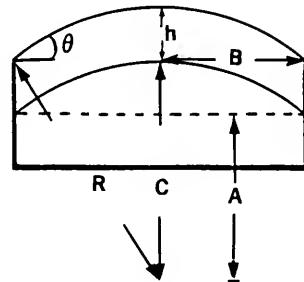
In order to calculate the volume of the unit cell at the height between A and C, V_{AC} , a sub unit cell which is 1/12 of the hexagonal unit cell is considered (Figure 49a and 49b). This volume can be calculated by integrating the cross sectional area at z, $A(z)$, with respect to z, where z is the arbitrary height in between A and C.



(a)



(b)



(c)

Figure 48. Unit Cell Structure used for Derivation of the Critical Ratio for the Grooves in the Vertices :
 a) hexagonal unit cell with a spherical cap
 b) top view of the unit cell
 c) front view of the unit cell

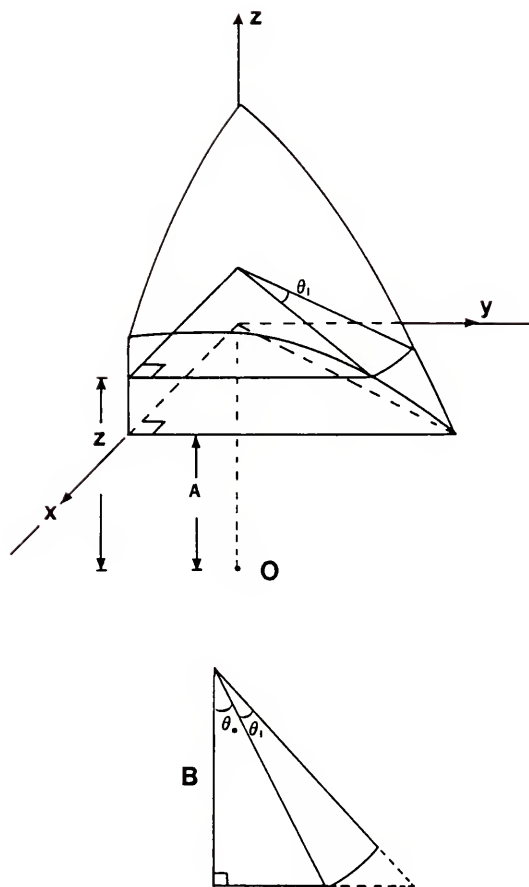


Figure 49. Sub Unit Cell Structure used for Calculating the Volume of the Grooves in the Vertices :
 a) sub unit cell which is $1/12$ of the unit cell
 b) cross section of the sub unit cell at the arbitrary height, z

The groove profile in the grain boundary in Figure 45c can be expressed by the equation of the circle, i.e.,

$$r_g^2 = y^2 + z^2 = r^2 \sin^2 \theta_0 + z^2.$$

Since $r_g^2 = R^2 - B^2$ and $r^2 = R^2 - z^2$,

$$R^2 - B^2 = r^2 \sin^2 \theta_0 + z^2 = (R^2 - z^2) \sin^2 \theta_0 + z^2.$$

Rearranging,

$$\sin^2 \theta_0 = 1 - B^2 / (R^2 - z^2)$$

or $\cos^2 \theta_0 = B^2 / (R^2 - z^2).$

The cross sectional area at z is the sum of the area of the triangle, A_t , and the area of the sector of the circle, A_s , as shown in Figure 49b. The area of the triangle is given by

$$A_t = 1/2 B (r \sin \theta_0) = 1/2 B (R^2 - B^2 - z^2)^{1/2}$$

and the area of the sector of the circle is given by

$$A_s = 1/2 r^2 \theta_1 = 1/2 r^2 (\pi/6 - \theta_0) = 1/2 (R^2 - z^2) (\pi/6 - \theta_0).$$

The total cross sectional area at z , $A(z)$, is written

$$\begin{aligned} A(z) &= A_t + A_s \\ &= 1/3 B (R^2 - B^2 - z^2)^{1/2} + 1/2 (R^2 - z^2) (\pi/6 - \theta_0) \\ &= 1/2 B (R^2 - z^2)^{1/2} \\ &\quad + \pi/12 (R^2 - z^2) - 1/2 (\pi/6 - \theta_0) \cos^{-1}(B^2 / (R^2 - z^2))^{1/2}. \end{aligned}$$

Integrating $A(z)$ with respect to z , yields the volume of the cell at z

$$V_{AC} = 6 \int_A^C [B (C^2 - z^2)^{1/2} + \{\pi/6 - \sec^{-1}(R^2 - z^2/B^2)^{1/2}\} (R^2 - z^2)] dz.$$

Let $u = z/B$. Then, $u = C/B$ at $z = C$, $u = A/B$ at $z = A$ and $dz = B du$.

Substituting for z with $u = z/B$,

$$V_{AC} = 6 B^3 \int_{A/B}^{C/B} \{(C/B)^2 - u^2\}^{1/2} + \{\pi/6 - \sec^{-1}(R^2/B^2 - u^2)^{1/2}\} \{(R/B)^2 - u^2\} du.$$

Note that A , C , and R can be expressed in terms of B and θ .

Let $A = xB$, $C = yB$ and $R = zB$. From the geometrical relations in Figure 49b and Figure 49c,

$$x = (1/\sin^2\theta - 4/3)^{1/2}, y = 1/\tan\theta \text{ and } z = 1/\sin\theta.$$

Substituting A , C and R ,

$$\begin{aligned} V_{AC} &= 6 B^3 [(y^2 - u^2)^{1/2} + \{\pi/6 - \sec^{-1}(z^2 - u^2)^{1/2}\} (z^2 - u^2)] du \\ &= 6 B^3 K \end{aligned}$$

$$\text{where } K = \int_x^y [(y^2 - u^2)^{1/2} + \{\pi/6 - \sec^{-1}(z^2 - u^2)^{1/2}\} (z^2 - u^2)] du.$$

Since K is function of θ only, the value of K can be determined by numerical integration.

Conservation of film volume requires that the sum of the volume of the unit cell between A and C , V_{AC} , and the volume of the spherical cap, V_C , must be equal to the volume of the film with thickness d , V_d .

$$V_d = 2\sqrt{3} B^2 d$$

and
$$V_{AC} + V_C = 6 B^3 K + \pi/(2-3\cos\theta + \cos^3\theta)/3 \sin^3\theta B^3.$$

Letting $V_{AC} + V_C = V_d$, the equilibrium groove depth at the grain boundary vertex is written

$$d = 1/2\sqrt{3} [6 K + (2 - 3 \cos\theta + \cos^3\theta)/3 \sin^3\theta] B.$$

The critical ratio of the grain size to film thickness for a film of thickness t , therefore, is obtained:

$$(t/B) < 1/2\sqrt{3} (6 K + (2 - 3 \cos\theta + \cos^3\theta)/3 \sin^3\theta) B$$

where
$$K = \int_x^y [(y^2-u^2)^{1/2} + \pi/6-\sec^{-1}(z^2-u^2)^{1/2} (z^2-u^2)] du.$$

The critical ratio, t/B , as a function of the groove angle is shown in Figure 50. Whereas the grooves do not reach the substrate in the region above the curve, the grooves do reach the substrate in the region below the curve.

As shown in Figure 50, the critical conditions are strongly dependent upon the size of the grain, the thickness of the film and the equilibrium groove angle. In a given groove angle, as the thickness of the film decreases or the grain size increases, the films are more susceptible to the instability caused by the grain boundary grooving. Similarly, in a given grain size and the thickness of the film, the film is more susceptible to the instability caused by grain boundary grooving as the equilibrium groove angle increases.

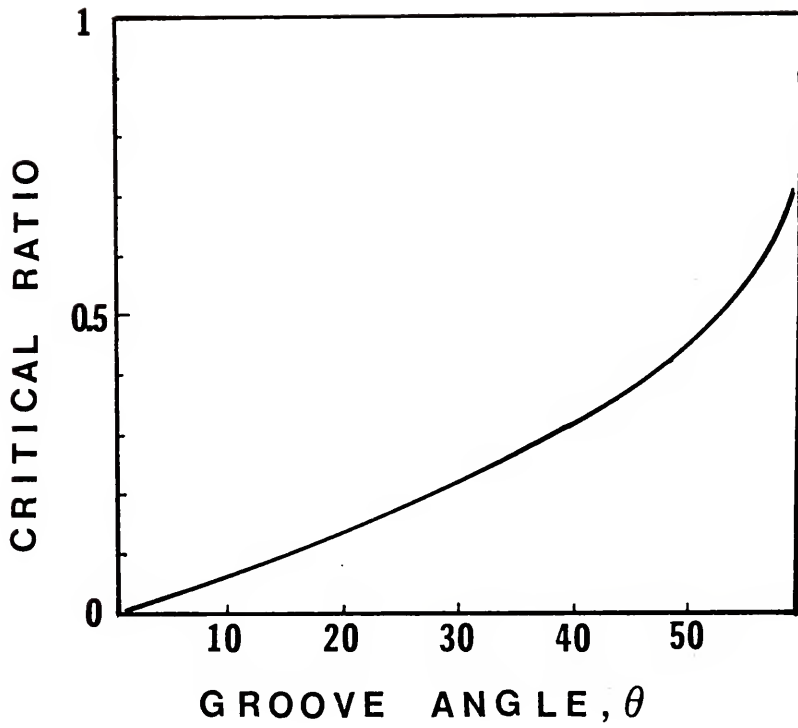


Figure 50. Critical Ratio of the Grain Size to Film Thickness Versus the Equilibrium Groove Angle

5.2. Parameters to Control the Groove Evolution in Au Thin Films

In order to apply the critical conditions to the grain boundary grooves observed in annealed Au films, the equilibrium groove angles at the annealing temperatures should be known. The equilibrium groove angle can be calculated using the equation, $\lambda_g = 2\lambda_s \sin \theta$, where λ_g and λ_s are the grain boundary energy and the surface energy of the grain.

Experimentally, the surface energy and the grain boundary energy are measured near the melting point in order to eliminate the dependence of these energies on crystallographic orientation. Also, both the surface energy and the grain boundary energy are temperature dependent. They decrease as temperature increases. Therefore, the rate of change of the surface energy and the rate of change of the grain boundary energy with temperature are also needed in order to calculate the equilibrium groove angle at the interested temperatures.

The experimental values of the surface energy and the grain boundary energy of gold at 1000 C and their rates of change with temperature reported as follows [112]:

$$\begin{aligned} \gamma_s &: 1.4 \text{ J/m}^2, \quad \partial \gamma_s / \partial T : - 0.43 \times 10^{-3} \text{ J/m}^2 \text{ C} \\ \gamma_g &: 0.378 \text{ J/m}^2, \quad \partial \gamma_g / \partial T : - 0.1 \times 10^{-3} \text{ J/m}^2 \text{ C}. \end{aligned}$$

Using these values, the surface energies, the grain boundary energies and the equilibrium groove angles at 300 C, 400 C and 500 C are calculated as shown in Table 8 for pure gold films.

The calculated critical ratio for an equilibrium angle of 8 degrees is about 0.07. This means that for a gold film of 700 Å the grain size

Table 8. Values of Surface Energy, Grain Boundary Energy and Equilibrium Groove Angle of Au at Various Temperatures

Temperature Degrees C	γ_s J/m ²	γ_g J/m ²	θ Degree
300	1.079	0.308	8.05
400	1.142	0.318	8.00
500	1.185	0.328	7.96

must be larger than $2\text{ }\mu\text{m}$ in diameter in order to have the groove reach the substrate and cause the hole formation.

Examination of the Au film annealed at $500\text{ }^{\circ}\text{C}$ with TEM (see Figure 5) shows that holes formed at grain boundary vertices of grains that are much smaller than $2\text{ }\mu\text{m}$; much larger grains sometimes had no hole formation at the vertices. This indicates that a higher critical ratio than theoretically predicted is valid for those smaller grains at which holes were observed at the vertices. Assuming the uniform thickness of the film, a higher critical ratio results from an increased groove angle. As shown in Figure 50, the critical ratio increases almost linearly with increasing groove angle at the lower angles and increases abruptly at the higher angles.

The critical ratio has been derived from the geometrical considerations under the assumptions of isotropic surface and grain boundary properties, uniform grain structure and no effects from defects and impurities. In real experimental conditions, these assumptions cannot be satisfied. Therefore, the evolution of the groove might be quite different from the theoretically predicted one.

The parameters which may determine the actual groove angle and thus the evolution of the grooves in Au film are considered below.

1) Anisotropic surface and grain boundary properties

The variation of surface energy and grain boundary energy with crystallographic orientation has been studied in FCC metals [113-117]. For gold, the lowest surface energy has been observed at an (111) orientation [64]. The extent of the surface energy anisotropy measured

by the ratio of the maximum free energy to the minimum free energy was about 1.2 [118]. Since the rate of change with temperature of surface energy is about 4 times that of grain boundary, the effect of anisotropy will be more significant at lower temperature.

If some grains had the combination of two energies such that the lowest surface energy is equilibrated with the highest grain boundary energy, the groove angle should be greater than that which is calculated using isotropic surface and grain boundary energies. With the lower surface energy of (111) orientation, about a 25 % increase in the groove angle and the critical ratio is calculated.

2) Impurities

The significant effect of impurities upon grain boundary grooving in Au thin films was reported by Goho [67]. The enhanced grain boundary grooving and hole formation observed during annealing were attributed to the reduction of the surface energy of gold by adding alkali elements. The effect of the adsorption sites of the adsorbate upon the surface energy of gold at high temperature has been also reported [119].

In addition to the change in the surface energy, impurity adsorption may also affect the rate of groove evolution by altering the kinetic conditions of the mass transport. Surface diffusion can be increased or decreased as a function of adsorbate type and form [120]. Oxygen and carbon are known to retard the surface diffusion of gold while alkali elements could enhance the surface diffusion of gold upon adsorption.

Gjostein reported the retention of small amounts impurities even during heating under hydrogen and ultra high vacuum [119]. If the gold films are locally contaminated or small amount impurities were adsorbed during the deposition and post-deposition process such as annealing, the evolution of the groove could be quite different, either enhanced or reduced, due to the adsorbed impurities.

3) Grain geometry

Microstructures of annealed Au films show that geometry of grains is not uniform. The shape and the size of the grains are not identical; there is a mixture of polygonal-shaped grains ranging from triangles to octahedrons. The effect of the shape of the grain on the groove evolution is depicted in Figure 51, where the critical ratio is plotted as a function of the shape of the unit cell. For a given groove angle, decreasing number of sides in the polygon produces a higher critical ratio.

The effect of size differences of grains is not clear. There may be some differences in the surface curvatures between two grains of different grain size. If so, an asymmetric groove profile could develop.

Due to the non-uniformity in the grain geometry, the critical ratio derived from the uniform, hexagonal unit cell may not be expected to apply to all the grains. Some grains, especially those that have a small number of sides such as triangles, may have a higher critical ratio.

4) Defects

A large number of defects such as vacancies and voids can be incorporated into thin films during deposition process [121]. For evaporated gold films, a high density of small voids ($< 50 \text{ \AA}$) was discovered by TEM [122-124]. These voids are believed to be formed primarily near the film-substrate interface.

During post-deposition processes such as annealing and current stressing the excess vacancies are readily annihilated by diffusion to various sinks available in the film, such as the free surface, grain boundaries and pre-existing voids [125,126].

Vacancy annihilation at the surface may cause the film thickness to be reduced, which is commonly called the thinning effect [127]. In this case the grain boundary groove could be deeper by the same amount as the reduction of the thickness. Vacancy annihilation at grain boundaries, particularly at groove tips, may upset the equilibrium groove angle and thus establish a driving force to promote further grooving. This is very similar to the accelerated grain boundary grooving induced by electromigration [128]. Vacancy annihilation at pre-existing voids at the film-substrate interface may cause the grain boundary grooving at this interface as well.

All these parameters may also affect the evolution of the groove. This suggests that the actual critical ratio for the instability of thin films due to grain boundary grooving depends upon many parameters. The reasonable prediction of the evolution of a grain boundary groove in polycrystalline thin films is evidently difficult.

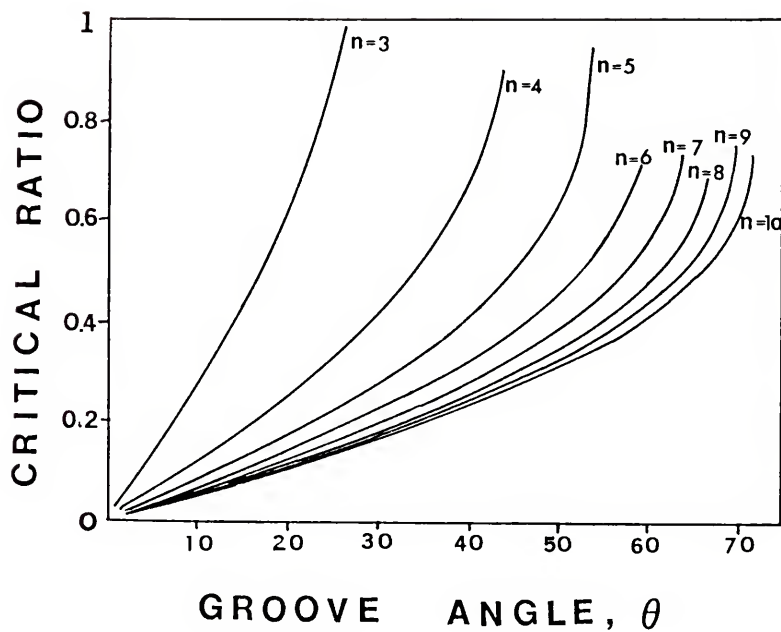


Figure 51. Critical Ratio for Various Shapes of the Unit Cell

CHAPTER 6 CONCLUSIONS

The present study on pure Au films and In/Au composite films leads to the following conclusions:

- 1) Pure Au films have grain boundary groovings upon heat treating.
- 2) Indium-gold films have no grain boundary groovings upon heat treating in air.
- 3) Indium is redistributed on gold films and forms In_2O_3 on the free surface and in the gold film during air heat treating.
- 4) Indium oxide, In_2O_3 , on the surface prevents grain boundary grooving in Au grains during heat treating.
- 5) Indium oxide, In_2O_3 , on the surface limits the mass transport process by capping the surface of gold film.
- 6) Indium oxide, In_2O_3 , in gold film, presumably residing along or near grain boundaries, impedes the grain growth by pinning the grain boundary migration.
- 7) The effect of indium underlays on the microstructure of gold is believed to be due to a randomization of the orientations of the grains, to a refinement of the grain size, to uniformity of the grain size distribution, and to roughening of the surface of gold films.

- 8) Indium oxide, In_2O_3 , on the surface was found to have polycrystalline grains whose mean grain size and thickness are 200 Å and 100 Å, respectively.
- 9) Indium is redistributed on gold films and forms a solid solution during hydrogen annealing.
- 10) The apparent difference in microstructures of annealed In/Au composite films examined by SEM and TEM results from the surface roughness of the films.
- 11) The critical ratio of the thickness to grain diameter for Au films was calculated to be 0.07 using experimental values of the surface energy and the grain boundary energy in the literature.

The above listed conclusions should be seen in the light of the reliability of gold metallizations in microelectronic circuits. As has been stated in the Introduction, gold films have a higher electro-transport related life time than aluminum metallizations. The main failure mechanism in pure gold films is, instead, caused by grain boundary grooving. This work has shown how grain boundary grooving can be significantly prevented and which mechanisms are responsible for this prevention. The next step for life time investigation needs to address itself whether or not only indium underlayers cause the beneficial effects described above, or whether or not other materials could be utilized likewise.

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BIOGRAPHICAL SKETCH

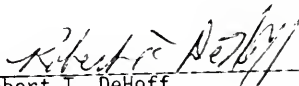
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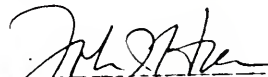
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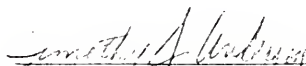
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